# Ultraviolet Spectra of Water from the Miramichi Watershed, New Brunswick

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# Ultraviolet Spectra of Water from the Miramichi Watershed, New Brunswick

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## ABSTRACT

Zitko, V., H. Collins, and J. Hunter. 2000. Ultraviolet spectra of water from the Miramichi watershed, New Brunswick. Can. Tech. Rep. Fish. Aquat. Sci. 2302: iii + 30 p.

Water samples from the Miramichi watershed were examined by ultraviolet (UV) spectrophotometry. A major component of dissolved organic matter is high molecular weight Natural Organic Matter (NOM, humic acid, fulvic acid), which may account for up to 50% of the UV absorbance. Average concentration of NOM, quantitated as humic acid, is 15 mg/L. Kraft lignin is also detectable in several samples. Concentration of NOM may be higher than 30 yr ago, but additional measurements are needed to confirm this. Preparations of NOM isolated from two samples have different UV as well as infrared (IR) spectra. Hexose-based polysaccharides were detected in a sample of foam and in a sample of sewage treatment plant effluent, whose Chemical Oxygen Demand (COD) is about 50 mg/L. Concentration of nonpolar organics in the runoff from Strawberry Marsh is considerably lower than 30 yr ago. Average concentration of nitrate in a small Miramichi-East stream, monitored for over 1 yr, is 13.7 mg/L. Floating whitish material, found in 1998 in the estuary, is a rancid lipid. Its source could not be determined.

## RÉSUMÉ

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Des échantillons d'eau provenant du bassin hydrographique de la Miramichi ont été examinés au moyen de la spectrophotométrie dans l'ultra-violet. La matière organique naturelle (MON) à poids moléculaire élevé est un composant principal de toute matière organique dissoute (MON, acide humique, acide fulvique); elle peut représenter jusqu'à 50 % de l'absorbance UV. La concentration moyenne de MON, quantifiée comme de l'acide humique, est de 15 mg / L. On a également décelé de la lignine de pâte de bois dans plusieurs échantillons. La concentration de MON peut être plus élevée qu'il y a trente ans, mais des mesures additionnelles seront nécessaires pour le confirmer. Des préparations de MON isolées à partir de deux échantillons présentaient des spectres UV et IR (infrarouge) différentes. Des polysaccharides à base d'hexose ont été décelés dans un échantillon de mousse et dans un échantillon des effluents de la station d'épuration des eaux usées, dont la demande chimique en oxygène (DCO) est d'environ 50 mg / L. Les concentrations de substances organiques apolaires dans les eaux de ruissellement du marais Strawberry sont beaucoup moins élevées qu'il y a trente ans. La concentration moyenne de nitrate dans un petit cours d'eau tributaire de la rivière Miramichi Est, qui a fait l'objet de relevés pendant plus d'un an, est de 13,7 mg / L. Une matière flottante blanchâtre, que l'on a retrouvée en 1998 dans l'estuaire, a été identifiée comme étant un lipide rance. Sa source n'a pu être déterminée.

## INTRODUCTION

Ultraviolet (UV) spectra of water samples from the Miramichi estuary, New Brunswick, were first measured 30 yr ago (Zitko et al. 1969; Elson et al. 1972). Since then, the situation in the estuary has changed considerably. A wood preserving plant closed July 15, 1986 (G. Lindsay, Environment Canada, Fredericton, NB, pers. commun.). The REPAP pulp mill installed an aerated lagoon as secondary treatment in 1971, a 3rd primary clarifier (two clarifiers were installed in 1967) and a settling basin in 1989. In 1993/94 the system was upgraded and consists of two clarifiers receiving effluent from wood rooms and a polymer settling aid, a defoamer, and a 3rd clarifier receiving effluent from the paper mill. All effluents are pumped to a settling basin and then to an aerated lagoon, where nutrients (urea and diammonium phosphate) are added to aid in the biodegradation (G. Lindsay, pers. commun.).

With the amalgamation of several Miramichi communities into the City of Miramichi it was determined to address the long-standing issue of inadequate sewage treatment. In January of 1998 the north side of the City of Miramichi benefited from the collection and treatment of wastewater at the Strawberry Marsh Sewage Treatment Plant (STP). Municipal officials selected an aerated lagoon system with four cells with capacity to include the newly connected communities of Nordin and Douglastown. The newly on-line system has a hydraulic retention time of 21 d and is subsequently discharged through a diffuser into the Miramichi River. The discharge is not chlorinated. Chathamhead and Nelson's sewage is "treated" in the lagoons in Chathamhead. This system is simply three lagoons with no aeration and the liner's (clay) effectiveness is very questionable. Chatham has an aeration ditch system which is too small to handle the received volumes. The by-pass flow is quite high. There is also a lagoon in Loggieville. The effectiveness of this lagoon is quite low, as the lagoon does not receive enough sewage.

General environmental awareness has increased substantially over the past 30 yr, as also signified by the existence and activities of the Miramichi River Environmental Assessment Committee (MREAC 1997). It was therefore of interest to measure again the UV spectra of at least a few water samples from the watershed. To illustrate the importance of observations and alertness for the quality of the environment, results of an investigation of a small stream, foam and floating material from the estuary, are also included.

UV spectra provide a fast and relatively inexpensive tool for an overall assessment of the concentration of organic compounds (see, for example, Hejzlar and Kopacek 1990; Brandstetter et al. 1996; Hanschmann et al. 1996; Matsche and Stumwöhrer 1996a,b). Correlations between the absorbance, usually at 254 nm ($A_{254}$) and dissolved organic carbon (DOC) or chemical oxygen demand (COD) have been established. Specific absorption coefficients determined by Hejzlar and Kopacek are given in Table 1, and those quoted in the same paper, in Table 2.

Table 1. COD specific absorption coefficients of different waters (Hejzlar and Kopacek 1990)

| Water | $A_{254}[m^2g^{-1}]$ | 95% confidence interval |
|---|---|---|
| Bog | 1.85 | 0.42 |
| Forest | 1.56 | 0.63 |
| River | 1.27 | 0.37 |
| Field | 1.01 | 0.36 |
| Impoundments | 1.00 | 0.37 |
| Lake | 0.89 | 0.19 |
| Groundwater | 0.73 | 0.37 |
| STP | 0.73 | 0.51 |
| STP | 0.67 | 0.15 |

Table 2. COD specific absorption coefficients quoted by Hejzlar and Kopacek (1990)

| Water | $A_{254}[m^2g^{-1}]$ |
|---|---|
| Polluted river | 1.37-1.43 |
| Pulp mill polluted river | 0.62-0.96 |
| River polluted with pulp mill and phenol effluents | 0.47-0.72 |
| Lakes or impoundments Finland | 1.05-1.72 |
| River Elbe | 1.67 |
| Waste waters | 0.41-0.43 |
| Ground waters | 0.78-0.96 |
| STP | 0.62-1.1 |
| Humic compunds isolated from soil | 1.94-2.45 |

Matsche and Stumwöhrer (1996) found the following relationship between COD and absorbance at 260 nm for municipal waste water treatment plants (STPs) in Austria:

$$COD\ [mg/L] = 136 * A_{260}\ [cm^{-1}] + 14 \quad [1]$$

Brandstetter et al. (1996) reported the relationship [2] for DOC and $A_{254}$ for natural waters:

$$DOC\ [mg/L] = 44.9 * A_{254}[cm^{-1}] + 1 \quad [2]$$

UV spectra may be deconvoluted by expressing them as mixtures of spectra of standards such as NOM, phenols, detergents, nitrates, etc. (Thomas et al. 1996, El Khorassani et al. 1999).

## MATERIALS AND METHODS

One-liter water samples were collected. A set of freshwater samples (samples M, Table 9) was collected on July 6, 1999 from the water surface. The initial set of water samples from the estuary was collected on July 13-14, 1999 from a 14-ft Delta Inflatable boat with a 25-hp motor, moving against the falling tide. Water was sampled at surface and at 1 m depth (samples 1-24, Table 9). Subsequently, water samples were obtained from a canoe along two transects in the estuary on August 13, 1999 (samples MI and ON, Table 9), and from the 'Chemical Creek' (samples 'CC'). The latter were taken at hourly intervals, starting 3 h before the low tide. Stations 11, 14, 20 and 22 were re-sampled on October 4 and station 22 again on October 7, 1999, since the previous sample was broken in transit. A sample of the Miramichi STP effluent was obtained on October 26, 1999. A 4-L water sample (MP) was collected at Middle Island on November 30, 1999. The samples were kept on ice, transported to the Biological Station within 48 h, where they were kept at 4°C in a cold room.

The UV spectra of the samples were measured from 200-350 nm, within 48 h after arrival. Water samples from the transects and from Chemical Creek were subsequently extracted with dichloromethane (30 mL/L) on magnetic stirrers for 2 h. The extracts were dried by sodium sulfate, evaporated to dryness on a rotary evaporator and weighed. Then they were dissolved in spectrograde hexane, combined and their spectra from 200-700 nm were determined.

Water from a small stream at the Miramichi-East airport was sampled sporadically from July 1998 until August 1999 (see Table 8 for dates). The samples were processed as described. Concentration of nitrate was calculated from the formula [3]. Testing for $Fe^{2+}$ was carried out by the reaction with 1,10-phenanthroline (Feigl 1958).

$$C_{NO3}\ [mg/L] = (A_{220} - 0.0625)/0.0613 \quad [3]$$

Foam was collected in September 1998, condensed by freezing and the liquid was dialyzed through a Spectra/Por CE Molecularporous membrane (Spectrum Medical Industries, Inc., Houston, TX 77043-4716, U.S.A.), diameter 10 mm and molecular weight cutoff 1000 dalton. A precipitate, formed in the high-molecular weight fraction, was centrifuged off, and both the supernatant and the precipitate were freeze-dried.

An 'unusual' whitish floating material was collected by a fisherman on August 9, 1998, about 100 m from shore near Neguac. Denis Daigle (NB Department of the Environment) passed on the material to us. The material was extracted with dichloromethane; solids suspended in the extract were collected by centrifugation. The extract was evaporated to dryness and the residue was examined by infrared (IR) spectrophotometry and by thin layer chromatography (TLC). The centrifuged-off solids were air-dried and examined by IR and by the biuret reaction. The biuret reagent for the determination of proteins was prepared as described (Dawson et al. 1969).

A portion of the STP effluent was dialyzed as described above and its UV spectrum was determined as well.

Standards of humic acid, Humex A and Humex B were a gift from Dr. E.T. Gjessing (Agder College, 4604 Kristiansand, Norway). High molecular weight (>1000 dalton) kraft lignin was isolated in 1992 from REPAP Miramichi effluent by dialysis and freeze-drying as described above. Spectrum of the whole effluent, determined at that time, is included for comparison. A high molecular weight fraction of the Miramichi Natural Organic Matter (NOM) was isolated from combined water samples M5 and M7 (Table 9) by concentrating the combined samples (approximately 1.8 L) to 50 mL, dialysis, and freeze drying. Additional NOM (MP) was isolated from the sample collected at Middle Island on November 30, 1999.

To obtain a relationship beteween UV spectra and salinity, seawater from the Biological Station's system was diluted with distilled water to

yield water samples with salinities ranging from 3 to 28 ppth and their UV spectra were measured, to give the formula [1].

Test for sugars by concentrated sulfuric acid (Zitko and Rosik 1961) was performed by overlaying 5 mL of concentrated sulfuric acid by 1 mL of distilled water or of the tested solution in a glass-stoppered 15 mL centrifuge tube. If the investigated material was a solid, insoluble in water, a trace of it was added to the aqueous layer, and the contents were mixed carefully (watch for heat generation, release pressure carefully, protect eyes!!!). The centrifuge tubes were heated for 5 min in boiling water and cooled to room temperature. UV spectra were scanned from 200-360 nm against the sulfuric acid blank. D-Glucose, D-arabinose, and D-glucuronic acid were used to prepare the calibration curves in the concentration range from 5-22 mg/L. Spectra of kraft lignin and NOM were determined as well.

To estimate the concentrations of NOM and pulp mill effluent in the samples, the calibration coefficients matrix **k** was calculated from the spectra of mixtures containing humic acid Humex A at 12.5, 18.7 and 25.0 mg/L, and kraft lignin at 4.4, 8.8, and 17.6 mg/L. Spectra in the interval 230–320 nm were used. The calculations were based on the equation

**Absorbance = k * concentration** [4]

From [4]

**k = Absorbance * concentration' *** inv(**concentration*concentration'**)

where **concentration'** = transpose of **concentration**, and 'inv' indicates inverted matrix.

With **k** determined on the standard mixtures, the concentration of humic acid and kraft lignin is calculated from the UV spectra by the least squares procedure:

**Calculated concentration = k \ measured absorbance ,** [5]

where '\' stands for the least squares calculation (see Matlab, below).

Deconvolution of spectra into components, based on the principle suggested by Thomas et al. (1996), was calculated according to equation [6], as outlined in [4] and [5]. The matrix dimensions of equations [4]-[6] are in Table 3.

Table 3. Matrix dimensions.

| Matrix | Rows | Column |
|---|---|---|
| Absorbance | Wavelengths[a] | Samples[b] |
| K | Wavelengths | 2 |
| Concentration | 2 | Samples |
| Spectra | Wavelengths | Samples |
| Components | Wavelengths | Components[c] |
| Proportions | Components | Samples |

[a]wavelength = 46; [b]samples = 9; [c]components = 2

**Spectra = Components * Proportions** [6]

Salinity was estimated from the absorbance at 210 nm ($A_{210}$) according to the equation

Salinity [ppth] = $18.404 * A_{210} - 2.17$ [7]

The value of $A_{210}$ was in turn corrected for the absorbance of NOM (Humex A) according to equation [8]

$A_{210} = 1.592 * A_{250}$ [8]

A Hewlett-Packard Diode Array spectrophotometer Model 8452A with a 2 nm resolution was used to scan the spectra. Infrared (IR) spectra were determined by a Perkin-Elmer Model 700 spectrophotometer in KBr pellets for NOM and neat for the lipid sample.

Thin layer chromatography was carried out on Whatman Silica Gel 150A, K5F, 5 x 20 cm plates, developed in petroleum ether-diethyl ether- acetic acid 80:40:1. The spots were visualized by charring with 60% sulfuric acid.

Matlab (The MathWorks Inc., Natick, MA 01760, USA), Excel 97 (Microsoft), and Quattro Pro (Borland International) software were used for data processing. First derivative spectra were calculated according to Savitzky and Golay (1964). Spectra scaled to a sum of absorbancies = 1, centered (mean =0) and scaled to standard deviation = 1, were analyzed by Principal Component Analysis (PCA, see, for example, Zitko 1994) by using PLS 2.0 Toolbox (Wise and Gallagher 1998). The projections on the plane of the first two principal components (score plot) were examined.

## RESULTS AND DISCUSSION

### UV SPECTRA

Typical UV spectra are presented in Fig. 1. A sharp increase in UV absorbance at wavelengths below 220 nm is caused by bromide present in sea water. Fresh water absorbs UV light below 220 nm much less than seawater. Natural organic matter (NOM), mostly humic and fulvic acid, many organic contaminants, nitrite and nitrate cause an increase in absorbance at wavelengths below 220 nm. In the Middle Island preparative sample MP, about 50% of the absorbance is caused by compounds with molecular weight below 1000 dalton (Fig.1, insert).

For a quick overview, values of $100*A_{250}$ are presented in Fig. 2 (see Fig. 3 for the locations of the stations and Table 9 for additional details). The $100*A_{250}$ values increase from 12-15 in the Sheldrake Island–Bartibog area to about 20-22 starting at Middle Island and, with a few exceptions, remain at this level. In sample 11, the absorbance at surface was much higher than at 1 m depth, but this difference was not observed on re-sampling (insert, Fig.2). Only at station 14 the absorbance of water at 1m depth was considerably higher than that of the surface water, but, again, this has not occurred on re-sampling. As can be seen from different values of $A_{200}$ , shown for samples at station 11, the stage of the tide was different. These differences emphasize the importance of sampling at well-defined stages of the tidal cycle and the need for simultaneous measurements of salinity.

As mentioned in the Introduction and also shown in Table 4, the intensity of UV absorption by NOM varies from preparation to preparation and the difference between the two Miramichi NOM preparations (M5&7 and MP) indicates that seasonal variations may have to be considered as well.

The $A_{250}$ values as well as the estimated concentrations of NOM for all samples are presented in Table 5.The calculations are based on $A_{250}$ of Humex A, since the quantities of NOM isolated from Miramichi water (M5&7 and MP) are too small to maintain as reference standards. However, most of the NOM appears to be of molecular weight below 1000 dalton. Sample MP, containing NOM at 25.7 mg/L as Humex A (Table 5), yielded preparatively only 6.2 mg/L of NOM with molecular weight > 1000 dalton, divided approximately equally between humic and fulvic acid.

Table 4. Calibration parameters for NOM and kraft lignin for absorbance at 250 nm ($A_{250}$)

| Sample | Water | Intercept $cm^{-1}$ | Slope $L\ cm^{-1}\ mg^{-1}$ |
|---|---|---|---|
| Humex A | distd | 0.039 | 0.0124 |
| | sea | 0.069 | 0.0124 |
| Humex B | distd | 0.041 | 0.0137 |
| | sea | 0.070 | 0.0140 |
| Middle Island | distd | 0.043 | 0.0133 |
| | sea | 0.100 | 0.0131 |
| M5&7 | distd | 0.043 | 0.0052 |
| Kraft | sea | 0.105 | 0.0158 |

The concentration of NOM was higher in the Northwest Miramichi during the original sampling, but the opposite was observed at two stations in October (Table 5, stations 20 and 22).

Water samples taken in the estuary transects (Table 9, samples ON and MI, Table 5) indicate that the absorbancies are fairly constant across the estuary. Absorbance increases with time (falling tide) in the discharge from Chemical Creek (Table 9, samples CC, Table 5).

In comparison with the data from 30 yr ago (Elson et al. 1972, Fig. 4, 5), it appears that the absorbance in middle and upper estuary is now higher: in 1969, in the City of Miramichi area, the $100*A_{250}$ values were about 15-20, as compared to 20-22 or higher, observed in 1999.

Unfortunately, salinity was not determined in the 1999 samples and was only estimated. According to the estimates, the salinity in the area of the City of Miramichi in the 1999 samples was generally the same in the 1969 samples. Consequently, the elevated concentrations of organic matter, observed in 1999 are not likely caused by sampling at a different stage of the tidal cycle. However, additional measurements, combined with those of salinity, at different stages of the tidal cycle, and at different seasons and fresh water inputs are needed to confirm this conclusion.

Table 5. Absorbance at 250 nm ($A_{250}$, $cm^{-1}$) and concentration of natural organic matter (NOM, mg/L), quantitated as Humex A, in the Estuary (E), Lower Estuary (LE), Southwest (SW), and the Northwest (NW) Miramichi

| Station | Location | A250 | NOM,mg/L | Station | Location | A250 | NOM,mg/L |
|---|---|---|---|---|---|---|---|
| 1a | E | 0.121 | 4.2 | 21a | SW | 0.192 | 9.9 |
| 1b | E | 0.116 | 3.8 | 21b | SW | 0.186 | 9.4 |
| 2a | E | 0.144 | 6.0 | 22a | SW | 0.181 | 9.0 |
| 2b | E | 0.143 | 6.0 | 22b | SW | 0.181 | 9.0 |
| 3a | E | 0.144 | 6.0 | o622b | SW | 0.405 | 27.1 |
| 3b | E | 0.144 | 6.0 | o822a | SW | 0.399 | 26.6 |
| 4a | E | 0.144 | 6.0 | 0822b | SW | 0.405 | 27.1 |
| 4b | E | 0.144 | 6.0 | 23a | SW | 0.188 | 9.6 |
| 5a | E | 0.197 | 10.3 | 23b | SW | 0.192 | 9.9 |
| 5b | E | 0.186 | 9.4 | 25a | SW | 0.189 | 9.7 |
| 6a | E | 0.182 | 9.1 | 25b | SW | 0.211 | 11.5 |
| 6b | E | 0.178 | 8.8 | m1 | LE | 0.163 | 7.6 |
| 7a | E | 0.201 | 10.6 | m2 | LE | 0.331 | 21.1 |
| 7b | E | 0.185 | 9.4 | m3 | NW | 0.192 | 9.9 |
| 8a | E | 0.220 | 12.2 | m5 | NW | 0.184 | 9.3 |
| 8b | E | 0.199 | 10.5 | m6 | NW | 0.296 | 18.3 |
| 9a | E | 0.204 | 10.9 | m7 | SW | 0.184 | 9.3 |
| 9b | E | 0.210 | 11.4 | on1s | E | 0.21 | 11.4 |
| 10a | E | 0.212 | 11.5 | on2s | E | 0.218 | 12.0 |
| 10b | E | 0.203 | 10.8 | on3n | E | 0.215 | 11.8 |
| 12a | E | 0.230 | 13.0 | on4n | E | 0.217 | 11.9 |
| 12b | E | 0.222 | 12.3 | mi1s | E | 0.163 | 7.6 |
| 13a | E | 0.242 | 14.0 | mi2s | E | 0.173 | 8.4 |
| 13b | E | 0.226 | 12.7 | mi3n | E | 0.172 | 8.3 |
| 15a | E | 0.204 | 10.9 | mi4n | E | 0.168 | 8.0 |
| 15b | E | 0.214 | 11.7 | cc1 | E | 0.234 | 13.3 |
| 16a | E | 0.317 | 20.0 | cc2 | E | 0.245 | 14.2 |
| 16b | E | 0.284 | 17.3 | cc3 | E | 0.253 | 14.8 |
| 17a | NW | 0.287 | 17.6 | 11a | E | 0.369 | 24.2 |
| 17b | NW | 0.294 | 18.1 | 11b | E | 0.218 | 12.0 |
| 18a | NW | 0.230 | 13.0 | o611a | E | 0.466 | 32.0 |
| 18b | NW | 0.231 | 13.1 | o611b | E | 0.471 | 32.4 |
| 19a | NW | 0.334 | 21.4 | 14a | E | 0.224 | 12.5 |
| 19b | NW | 0.318 | 20.1 | 14b | E | 0.306 | 19.1 |
| 20a | NW | 0.587 | 41.8 | o614a | E | 0.47 | 32.3 |
| 20b | NW | 0.317 | 20.0 | o614b | E | 0.472 | 32.5 |
| o520a | NW | 0.299 | 18.5 | o614a | E | 0.47 | 32.3 |
| o520b | NW | 0.302 | 18.8 | o614b | E | 0.472 | 32.5 |
| o620a | NW | 0.289 | 17.7 | MP | E | 0.350 | 22.7 |
| o620b | NW | 0.292 | 18.0 | | | | |

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Too few measurements were carried out in the fresh water end of the estuary in 1969, but it appears that the concentration of NOM, now entering the estuary, may be higher than in 1969. Regular monitoring, combined with discharge data, are needed to confirm this observation. The absorbance is about the same as in 1969 at the mouth of the estuary.

In 1969, the $100*A_{230}$ value of the effluent from Chemical Creek, collected at a falling tide, increased from 18 to 27; however, at that time the effluent contained chloroform-extractable compounds at 24 mg/L (Zitko et al. 1969). The current effluent contained only a trace of dichloromethane-extractable organics (1.69 mg/L). Water samples from the transects contained similar organics at 1.83 and 2.22 mg/L (mean of 4 samples), in the MI and the ON transect, respectively. The UV/visible spectra of the extracts indicated the presence of phaeophytin, a chlorophyll decomposition product (Fig. 6).

## SPECTRAL PATTERNS, NOM (HUMIC ACID, FULVIC ACID) AND KRAFT LIGNIN IN THE SAMPLES

Projections of scaled (sum of absorbancies = 1) 230-320 nm spectra on the plane of the first two principal components are used to present similarities and differences among the spectra in more detail (Fig. 7). In these projections, the effect of concentration is to a large extent eliminated by the scaling, and the effect of varying salinity is avoided by not using wavelengths below 230 nm. Similarity of the spectra is inversely proportional to the distance of their projections. The original samples 11a, 14b, 20a, and 22ab are outliers, and so are the foam (F), the REPAP 1992 effluent (E), and the high-molecular weight fraction of NOM from samples M5 and M7 (M5&7). The NOM (H), represented by Humex A, NOM from the Middle Island preparative sample (MP), and the STP effluent (W) are at the edge of the main cluster. Only six samples, 2b, 8b (just to the left of m1, shown only as '.' in Fig. 7), m1, 13a and 16ab, are relatively close to kraft lignin (K). This is in agreement with an earlier study showing a fairly rapid dispersion of the pulp mill effluent in the estuary (Whitney and Wilson 1968). Calculations according to [4], calibrated on mixtures of kraft lignin and humex A (Table 6), show the concentration of NOM and kraft lignin in these samples (Table 7). However, the spectra of Humex A, kraft lignin, and REPAP effluent are very similar and, consequently, the calculated concentrations must not be over-interpreted. As can be seen from the 1st derivative spectra, the spectrum of REPAP effluent, not considered in the calculations, is somewhat different from that of the kraft lignin (Fig.8). For spectra that differ very much from kraft lignin and Humex A mixtures, the calculations would result in meaningless values. Sample 16a, which is most similar to the effluent (Fig. 7) yields a negative concentration of NOM (Table 7).

Table 6. Concentration (mg/L) of kraft lignin and Humex A in calibration samples

| Actual | | Determined | |
|---|---|---|---|
| Kraft | Humex | Kraft | Humex |
| 4.4 | 12.5 | 6.7 | 12.0 |
| 8.8 | 12.5 | 9.7 | 12.6 |
| 17.6 | 12.5 | 18.7 | 12.0 |
| 4.4 | 18.7 | 6.0 | 17.4 |
| 8.8 | 18.7 | 7.5 | 20.2 |
| 17.6 | 18.7 | 16.9 | 19.6 |
| 4.4 | 25 | 3.6 | 25.8 |
| 8.8 | 25 | 8.5 | 24.5 |
| 17.6 | 25 | 16.8 | 24.2 |

Table 7. Concentration (mg/L) of kraft lignin and NOM (as Humex A) in Miramichi samples

| Station | Kraft | Humex A |
|---|---|---|
| 2b | 2.9 | 5.9 |
| 8b | 3.7 | 8.5 |
| m1 | 3.3 | 6.5 |
| 13a | 7.4 | 7.1 |
| 16a | 19.1 | -2.0 |
| 16b | 13.4 | 2.5 |

As can be seen from Fig. 7, there are differences in the spectra of the initial fresh water samples ('M' series'). It would be interesting to see how reproducible and stable are these differences. It may be of interest to study these matters in more detail. IR spectra of the two Miramichi NOM samples (Fig. 9) are different and the subject may be worth pursuing further. Atlantic salmon are known to 'home' on parent streams and NOM may be the streams' 'signature'. NOM also plays an important role in the fate and effects of heavy metals and hydophobic organic chemicals (see, for example, Zitko et al. 1972; McCarthy 1989; McCarthy et al. 1985; Landrum et al. 1987; and Haitzer et al. 1998, 1999). Consequently, more attention should be given to NOM in the Miramichi watershed.

The considerable difference between the Chemical Creek C1 , C2, and C3 spectra (Fig. 7) indicates leaching of some organics by water remaining for a longer time in the creek.

Scaled spectra of the condensed foam, the sewage plant effluent (STP) and the high-molecular weight NOM isolated from samples M5 and M7 are slightly different. The differences are better apparent in the respective 1st derivative spectra (Fig. 10). These differences may be large enough to attempt the deconvolution of spectra of water samples and calculations of concentrations in terms of STP effluent, NOM, etc. (see, for example,Thomas et al. 1996; El Khorassani et al. 1999).

## POLYSACCHARIDES IN MIRAMICHI WATER

Spectra of kraft lignin, Humex A, the Miramichi NOM (M5&7, MP), and glucose in sulfuric acid are presented in Fig. 11. As can be seen from the slight indication of a maximum at approximately 320 nm, kraft lignin, Humex A, and humic-type NOM may contain traces of hexose-based polysaccharides. On the other hand, both foam and STP contain these polysaccharides (maxima at 320 nm) and can be approximated by mixtures of NOM and glucose, calculated according to equation [6]. It appears from Fig. 12, that the foam is best approximated by a mixture of kraft lignin and glucose (spectrum K) in a ratio of 71 to 5. Mixtures of lignin or NOM and glucose approximate equally well STP in a ratio of approximately 25 to 3. The polysaccharide in STP is probably of bacterial origin. Similarly, high molecular weight NOM in STP may be of bacteria; origin. The formation of humic type substances by aquatic microorganisms has been reported (Claus et al. 1999) and may account for this type of NOM in the STP.

## NITRATE IN MIRAMICHI-EAST STREAM

This stream was brought to the attention of MREAC because of a thick 'mat' covering its bottom in the vicinity of the stream's source near the municipal airport. The mat consisted of 70% silt and 30 % organic matter. UV spectra of water from the stream show the presence of nitrate (Table 8; average spectrum, nitrate concentration 13.7 mg/L as $NO_3$, Fig. 13). With the exception of two samples (1 and 7, Fig. 14), the spectra show predominance of nitrate and differ only in nitrate concentration, increasing from left to right (Fig. 14, 15). It is quite unusual to encounter surface water with such a high concentration of nitrate. The origin may be a fertilizer runoff or a septic field discharge. Additional work is needed to determine the source. The presence of $Fe^{2+}$ was noticed in the first sample by a rapid appearance of yellow precipitate of ferric hydroxide. This indicated that the water must have been anoxic before coming to the surface. Later samples did not contain $Fe^{2+}$.

Table 8. Concentration of nitrate in Miramichi-East stream.

| Number | Date | NO3, mg/L |
|---|---|---|
| 1 | 30.07.98 | 13.3 |
| 2 | 14.08.98 | 14.9 |
| 3 | 14.08.98 | 15.5 |
| 4 | 17.08.98 | 11.1 |
| 5 | 19.08.98 | 11.9 |
| 6 | 21.08.98 | 10.9 |
| 7 | 24.08.98 | 20.4 |
| 8 | 27.08.98 | 14.4 |
| 9 | 31.08.98 | 11.9 |
| 10 | 02.09.98 | 11.6 |
| 11 | 8.10.98 | 12.0 |
| 12 | 17.06.99 | 10.6 |
| 13 | 17.06.99 | 15.7* |
| 14 | 13.07.99 | 14.1 |
| 15 | 28.07.99 | 12.8 |
| 16 | 17.08.99 | 18.7 |

* algal 'mat' supernatant.

## FLOATING LIPID

The whitish material was mostly soluble in dichloromethane. IR spectrum and TLC profile of the soluble fraction (Fig. 16) identify it as a rancid oil. The dichloromethane-insoluble fraction was identified as a protein, by biuret reaction. A possible source is rancid frying oil.

## SEWAGE TREATMENT PLANT (STP) EFFLUENT

The UV spectra of the effluent before and after dialysis are presented in Fig. 17. The dialysis removed salts and, consequently, primarily lowered the absorbance at the shorter wavelengths. From the equation [1], the COD is 50 and 47 mg/L for the original and for the dialyzed effluent, respectively.

Table 9. Sample information

| Sample | Time | Location | Latitude | Longitude | Temp. | $O_2$ | Date |
|---|---|---|---|---|---|---|---|
| M1 | 10:18 AM | Fins&Feathers | 47°06.782 | 065°23.193 | 17.5 | 9.5 | 7/6/99 |
| M2 | 10:43 AM | Johnson | 47°00.969 | 065°24.201 | 16.6 | 8.6 | 7/6/99 |
| M3 | 11:10 AM | Repap | 46°58.521 | 065°36.140 | 16.3 | 9.5 | 7/6/99 |
| M5 | 11:45 AM | NW Millstream | 46°68.458 | 065°41.633 | 18.8 | 10 | 7/6/99 |
| M6 | 12:22 PM | Fish Hatchery | 46°57.088 | 065°39.400 | 22.3 | 9.2 | 7/6/99 |
| M7 | 1:11 PM | Renous | 46°48.617 | 065°47.967 | 22.1 | 10 | 7/6/99 |
| 1-A 1-B | 6:41 AM | M58-West of Sheldrake | 46° 50.052 | 065° 46.148 | 18.3 | | 7/13/99 |
| 2-A 2-B | 7:07 AM | M61-West of Bartibog | 47°04.987 | 065°71.795 | 18.7 | | 7/13/99 |
| 3-A 3-B | 7:35 AM | M65-Off Gordon's Point | 47°04.705 | 065°23.447 | 18.7 | | 7/13/99 |
| 4-A 4-B | 8:00 AM | M68 | 47°03.886 | 065°25.143 | 18.6 | | 7/13/99 |
| 5-A 5-B | 8:25 AM | M73-off Middle Island | 47°03.265 | 065°27.469 | 19.4 | | 7/13/99 |
| 6-A 6-B | 8:43 AM | M76- | 47°02.210 | 065°28.102 | 19.4 | | 7/13/99 |
| 7-A 7-B | 9:20 AM | M64- | 47°01.185 | 065°29.512 | 19.7 | | 7/13/99 |
| 8-A 8-B | 10:34 AM | M90-Buoy | 47°00.913 | 065°31.796 | 20.1 | | 7/13/99 |
| 9-A 9-B | 9:47 AM | M95-Below Richie Wharf | 47°00.471 | 065°33.596 | 20.2 | | 7/13/99 |
| 10-A 10-B | 9:58 AM | M99-opp Newcastle Wharf | 47°00.067 | 065°33.521 | 20.1 | | 7/13/99 |
| 11-A 11-B | 10:10 AM | Mc10- | 46°59.045 | 065°33.682 | 20.1 | | 7/13/99 |
| 12-A 12-B | 10:21 AM | Mc24&25 | 46°58.789 | 065°34.865 | 20.3 | | 7/13/99 |
| 13-A 13-B | 10:33 AM | Mc35 off Repap Pup Mill | 46°57.972 | 065°35.528 | 20.4 | | 7/13/99 |
| 14-A 14-B | 11:01 AM | SW Mir@Repap | 46°58.617 | 065°33.473 | 20.6 | | 7/13/99 |
| 15-A 15-B | 10:48 AM | off Enclosure on SW Mir | 46°57.471 | 065°35.095 | 20.6 | | 7/13/99 |
| 16-A 16-B | 7:14 AM | off Repap Mill | 46°57.957 | 065°36.231 | 20.6 | 9.2 | 7/14/99 |
| 17-A 17-B | 7:29 AM | off west end of Eel groundNW | 46°57.650 | 065°38.180 | 20.6 | 9.8 | 7/14/99 |
| 18-A 18-B | 7:48 AM | Below Millstream NW | 46°57.790 | 065°42.040 | 20.5 | 10 | 7/14/99 |
| 19-A 19-B | 8:10 AM | Boom Point NW | 46°56.321 | 065°46.601 | 20.9 | 9.7 | 7/14/99 |
| 20-A 20-B | 8:28 AM | Sutherland's Brook NW | 46°56.345 | 065°49.104 | 21.1 | 9.4 | 7/14/99 |
| 21-A 21-B | 9:42 AM | Tip of Barnaby Island SW | 46°54.644 | 065°37.279 | 20.8 | 11 | 7/14/99 |
| 22-A 22-B | 10:08 AM | SW Mir off Frank's Resort | 46°52.678 | 065°39.792 | 21.1 | 10 | 7/14/99 |
| 23-A 23-B | 10:36 AM | Hackett's Brook SW Mir | 46°50.186 | 065°44.979 | 21.9 | 9.6 | 7/14/99 |
| 25-A 25-B | 11:00 AM | Quarryville Bridge | 46°49.668 | 065°47.250 | 22 | 10 | 7/14/99 |
| MI1S | 9:00 AM | Middle Island | 47°02.975 | 065°27.695 | 19.7 | 8.9 | 8/13/99 |
| MI2S | 9:05 AM | Middle Island | | | | | |
| MI3S | 9:10 AM | Middle Island | | | | | |
| MI4S | 9:15 AM | Middle Island | | | | | |
| ON1S | 9:35 AM | O'Neils | 47°00.720 | 065°32.399 | 20.1 | 9.1 | 8/13/99 |
| ON2S | 9:40 AM | O'Neils | | | | | |
| ON3N | 9:45 AM | O'Neils | | | | | |
| ON4N | 9:50 AM | O'Neils | | | | | |
| CC1 | | | | | | | |
| CC2 | | | | | | | |
| CC3 | 2:20 PM | Strawberry Marsh | 46°59.720 | 065°33.788 | | | 8/12/99 |

## CONCLUSIONS

The concentration of dissolved organic matter in the Miramichi City area may be higher than 30 yr ago; however, more detailed monitoring together with measurement of salinity and fresh water input are needed for a definitive conclusion. A major component is natural organic matter (NOM). Kraft lignin is also detectable and predominates at some stations. Since NOM may affect the behaviour of organic as well as inorganic contaminants, a more detailed study is warranted.

The high-molecular-weight fraction of the Miramichi STP effluent contains mixture of a hexose-based polysaccharide and humic-like NOM.

The concentration of non-polar organic matter in Chemical Creek is much lower than 30 years ago.

A small stream near the airport contains nitrate at about 14 mg/L.

A sample of foam contained mixture of a hexose-based polysaccharides and kraft lignin.

A whitish, string-like material consisted mostly of rancid lipid and also contained some protein. The source could not be determined.

Foam, unusual floating materials, slicks or spills should be sampled and investigated by chemical analyses.

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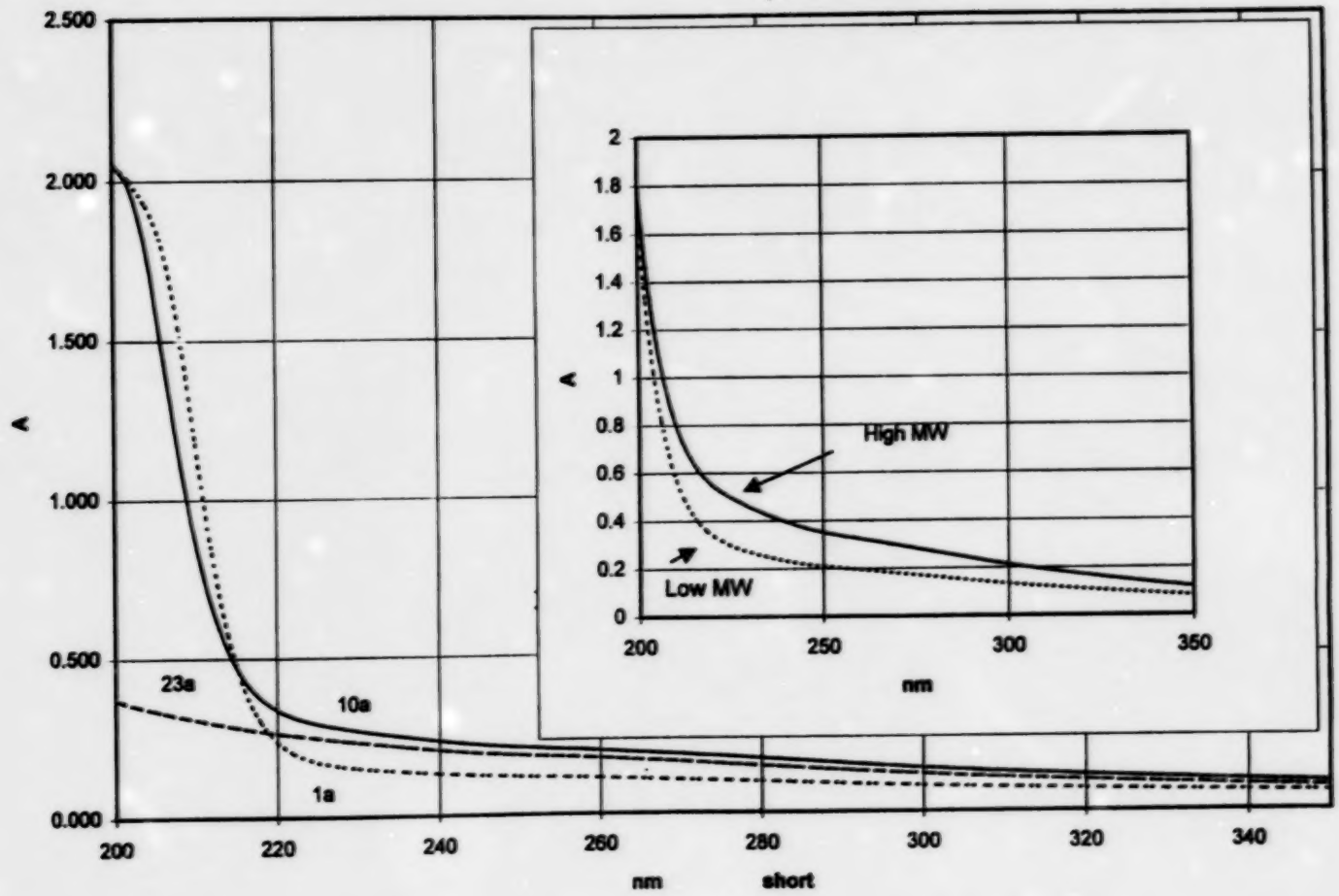


Fig.1. Typical ultraviolet (UV) spectra. On x-axis – wavelength in nm (nanometer, $10^{-9}$m), on y-axis – absorbance, $cm^{-1}$. 1a, 10a, 23a = sea, brackish, and fresh water, respectively. See Fig.3 and Table 9 for sampling locations. Insert: Spectrum of high (>1000 dalton) and low molecular weight fractions of sample MP.

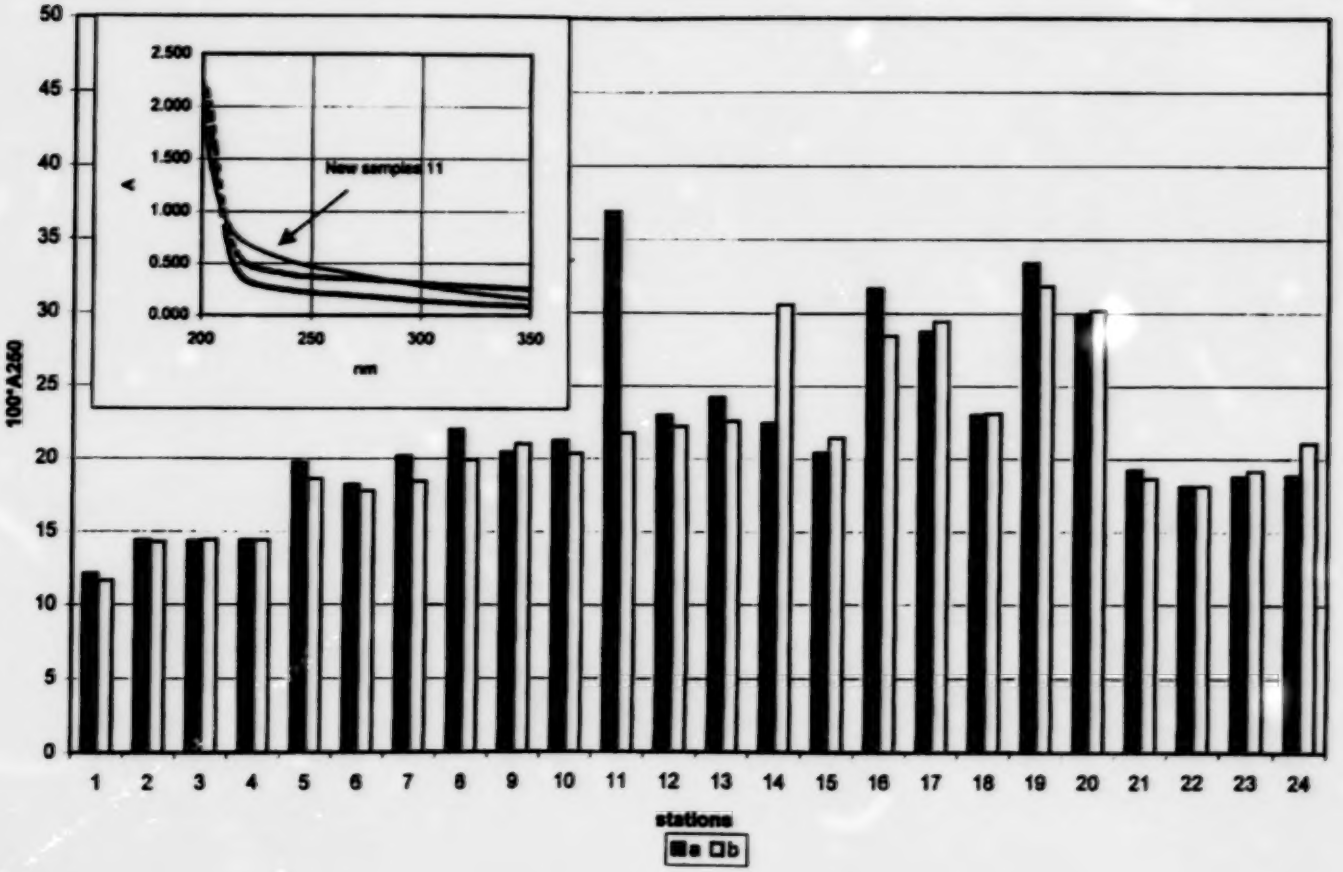


Fig.2. Absorbance at 250 nm ($A_{250}$), expressed as 100* $A_{250}$ , at stations in the estuary (see Fig.3 and Table 9 for sampling locations). Black bars – surface, white bars – 1m depth. Insert: Spectra of samples from station 11. No difference between samples a and b was observed on re-sampling.

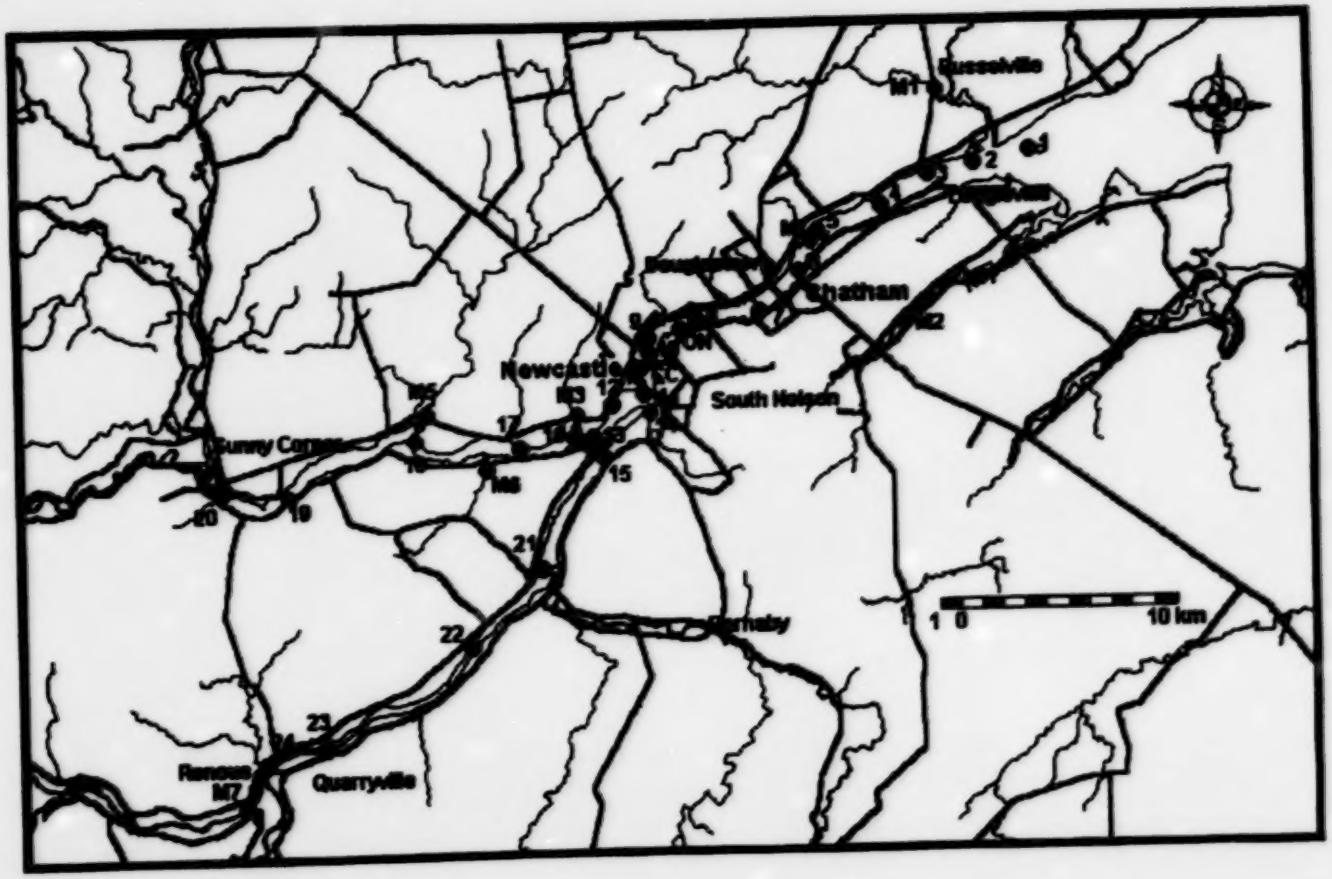


Fig. 3. Map of sampling locations. Use in conjunction with Table 9.

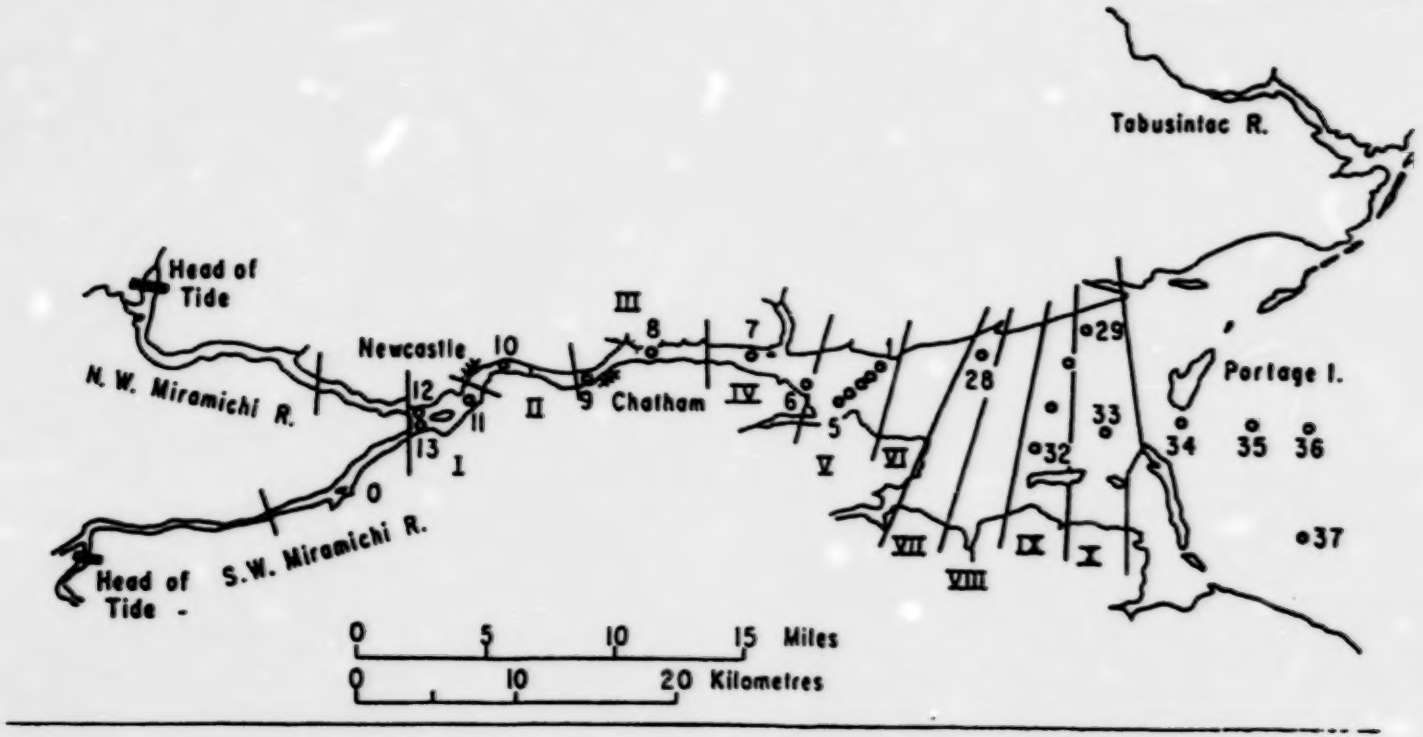


Fig.4. Sampling stations at the 1969 survey (Elson et al 1972).

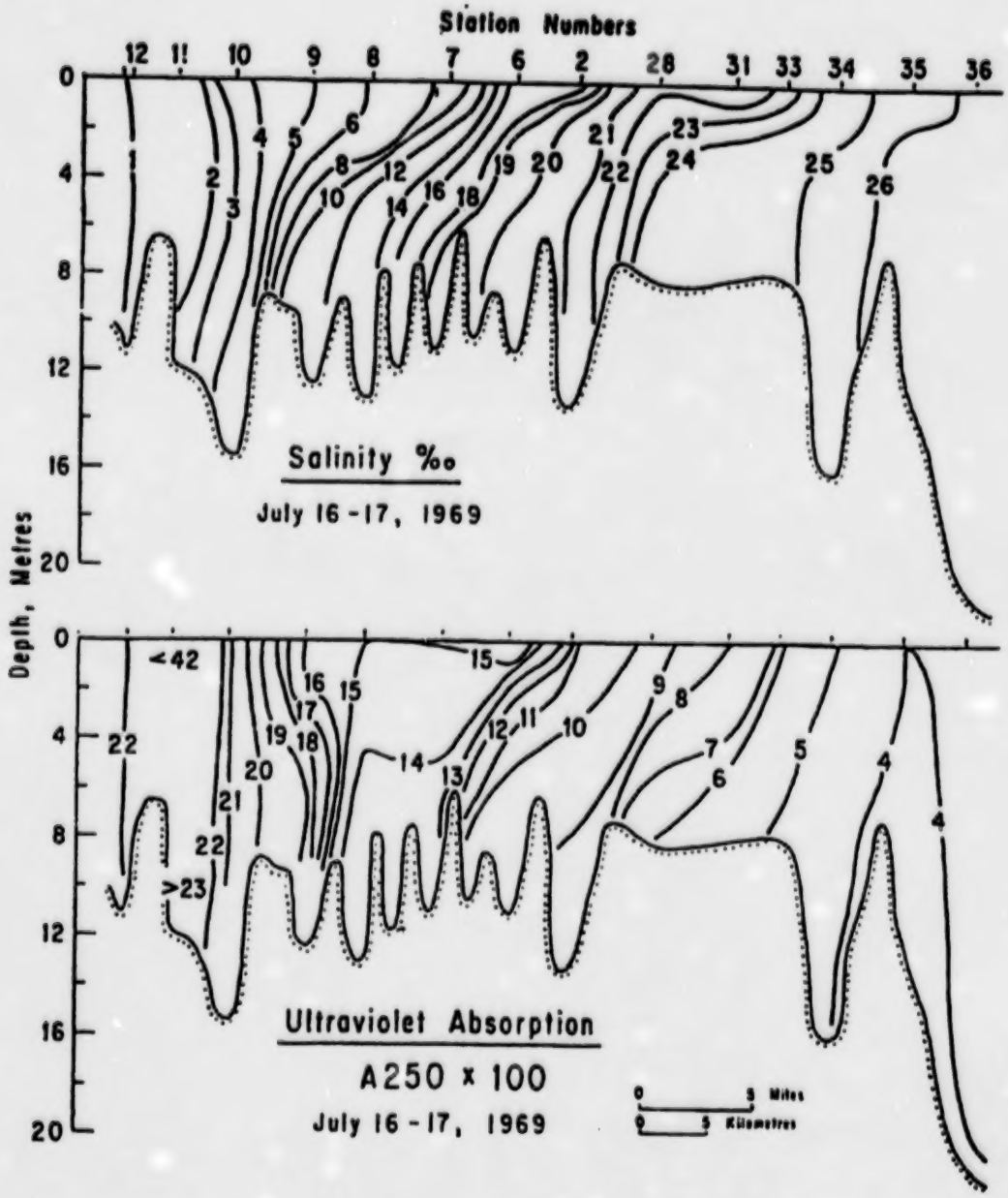
Station Numbers
12 11 10 9 8 7 6 2 28 31 33 34 35 36
Salinity ‰
July 16 - 17, 1969
Depth, Metres
Ultraviolet Absorption
A250 x 100
July 16 - 17, 1969
0 5 Miles
0 5 Kilometres

Fig.5. Salinity and 100* $A_{250}$ values during the 1969 survey (Elson et al 1972).

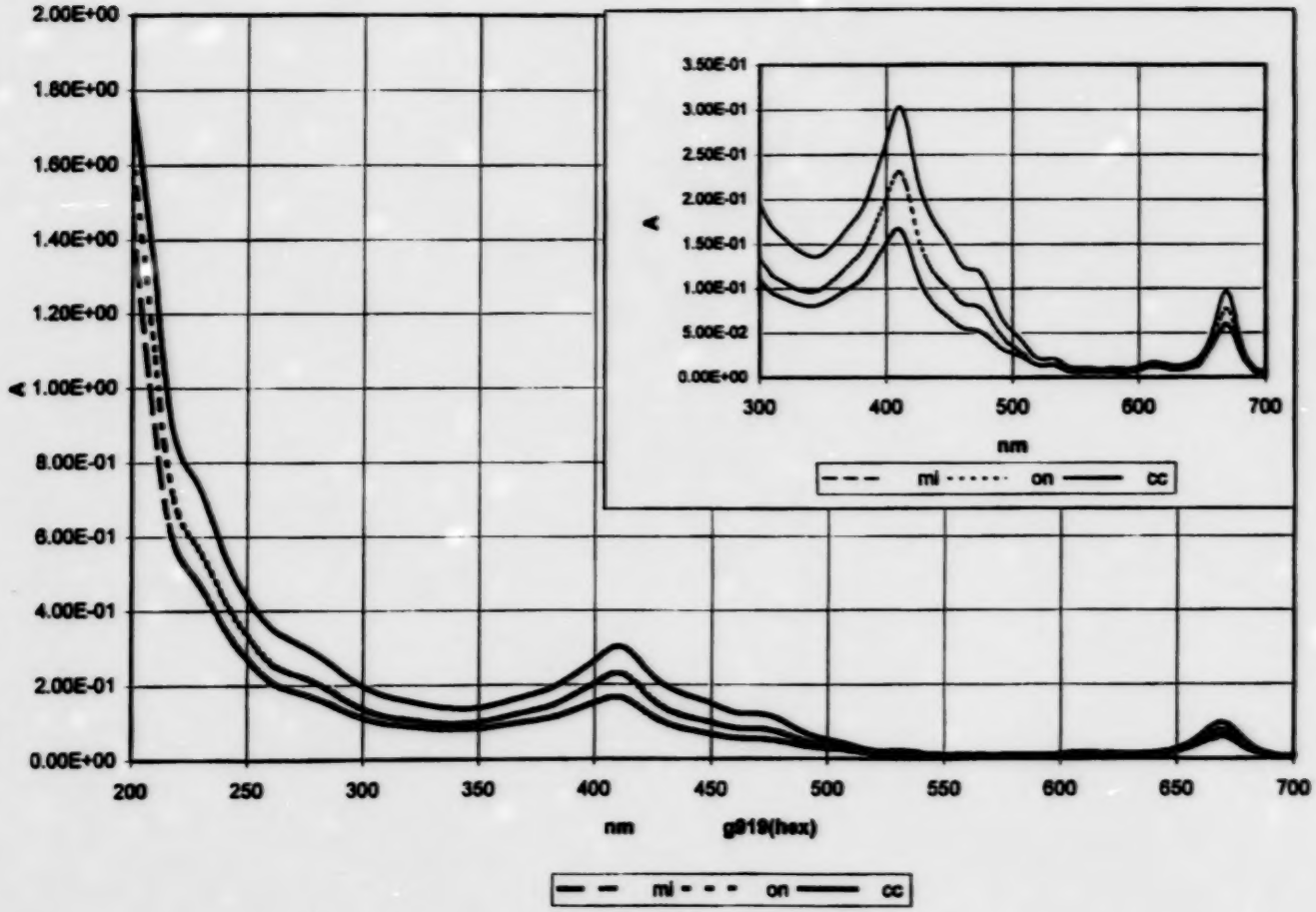


Fig.6. UV/visible spectra of dichloromethane extracts of combined transects and Chemical Creek samples, measured in hexane. Insert: enlarged 300 – 700 nm section.

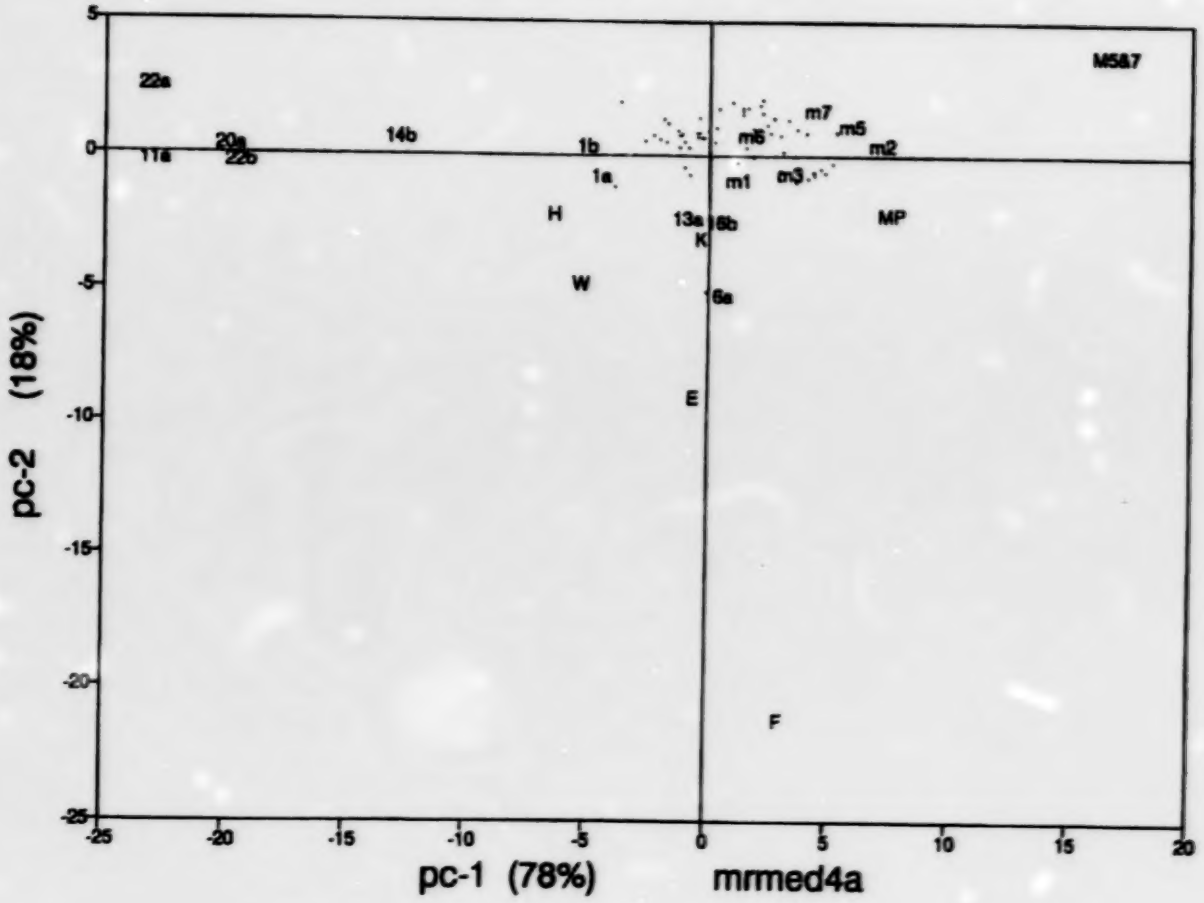


Fig. 7. UV spectra scaled to unit length and projected on the plane of the first two principal components. Similar spectra are located in proximity. See Fig.3 and Table 9 for sample identification. 'F','E','W','H','K', 'M5&7', and 'MP' are spectra of foam, 1992 REPAP effluent, STP effluent, Humex A, kraft lignin, M5&M7 NOM, and Middle Island NOM, respectively.

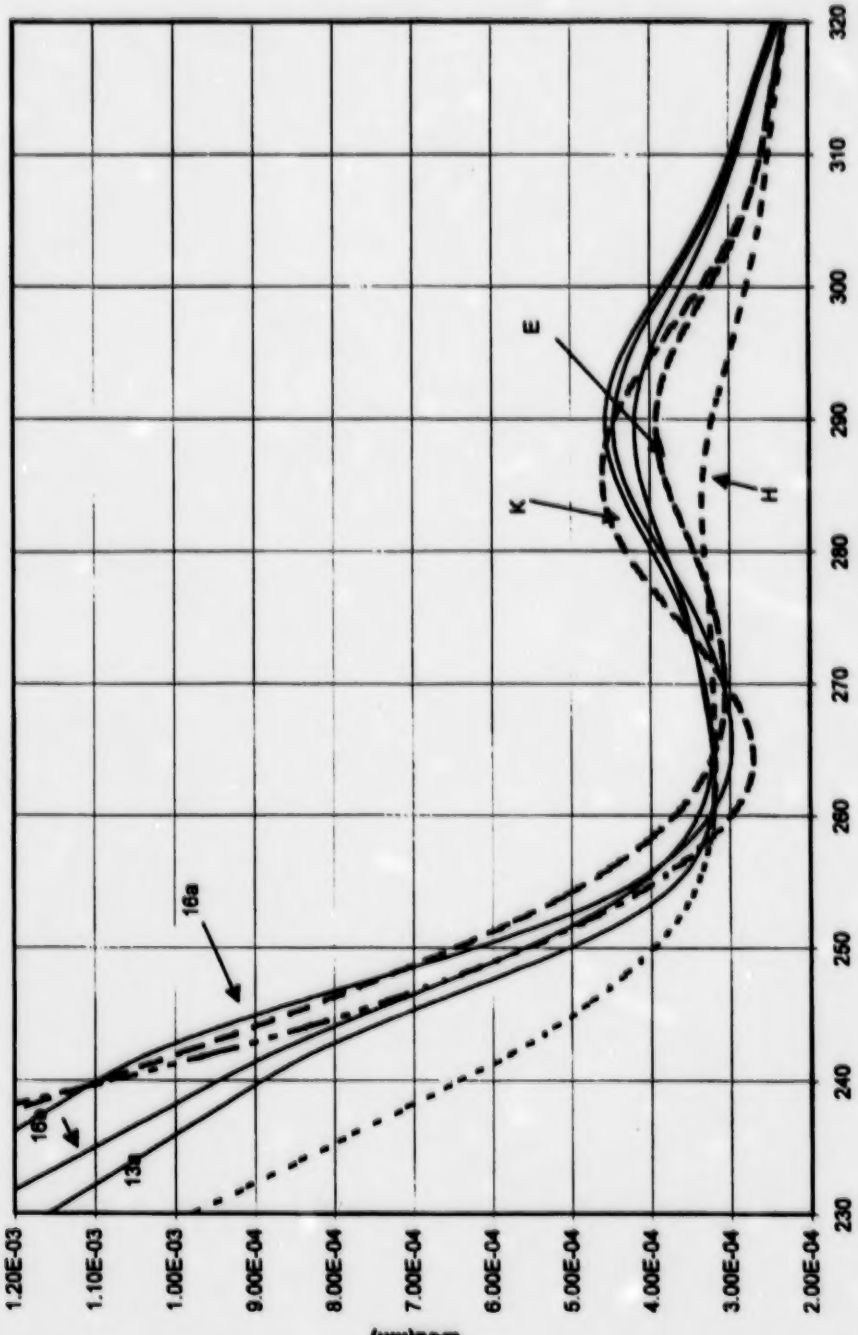


Fig. 8. 1st derivative spectra of 13a, 16a,b, kraft lignin, Humex A, and REPAP effluent.

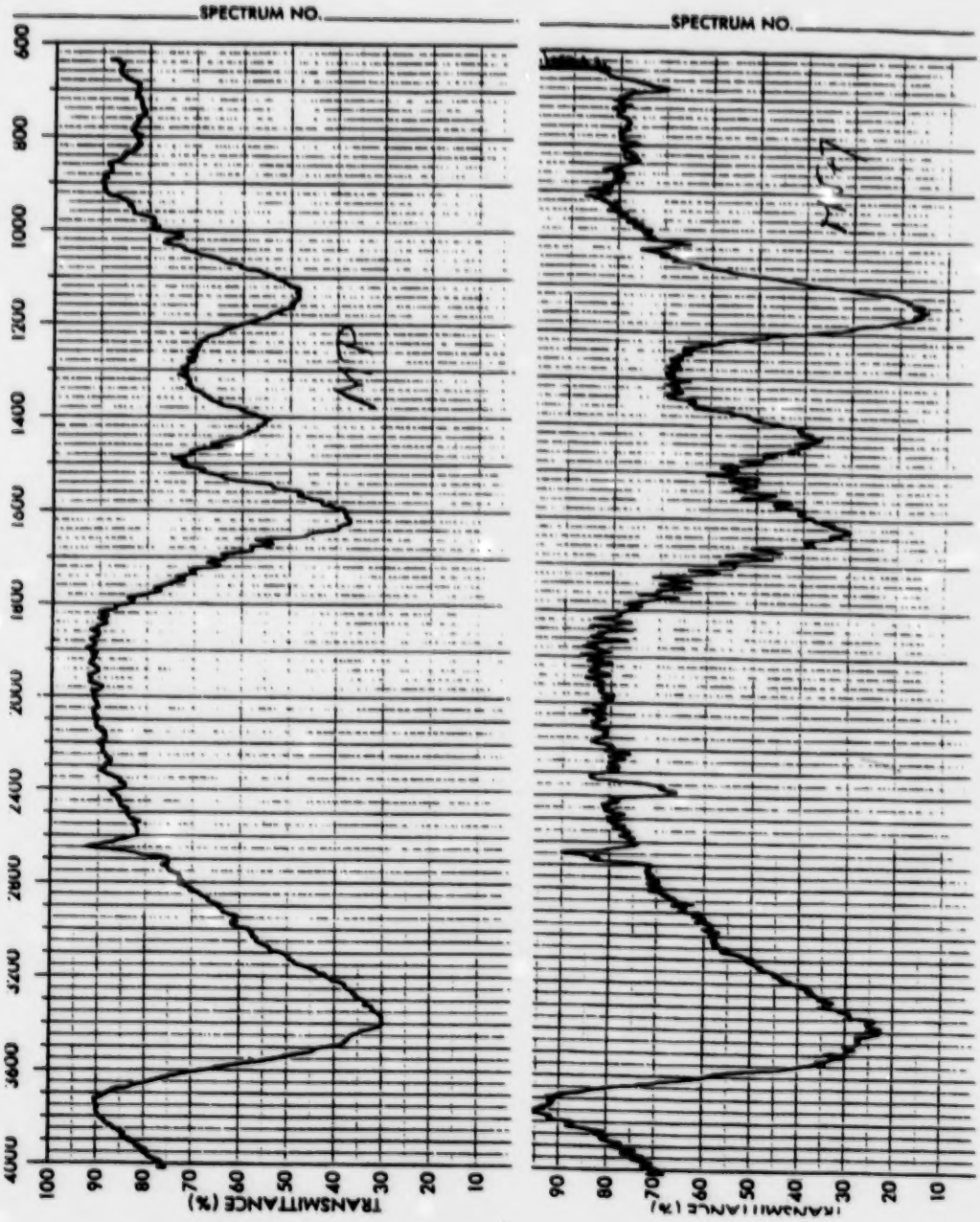


Fig. 9. Infrared (IR) spectra of Miramichi NOM.

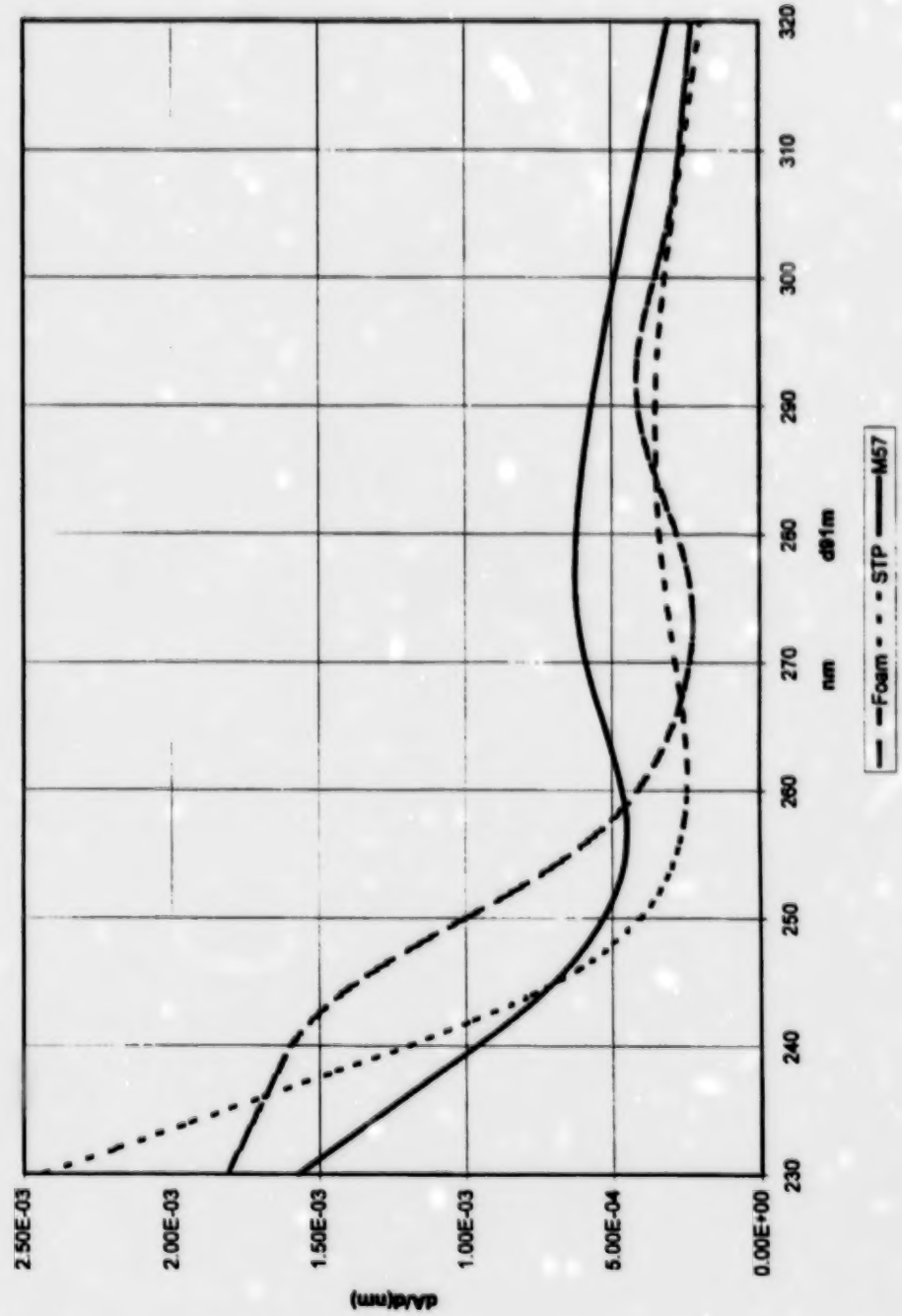


Fig. 10. 1st derivative spectra of foam, STP, and M5&M7 NOM.

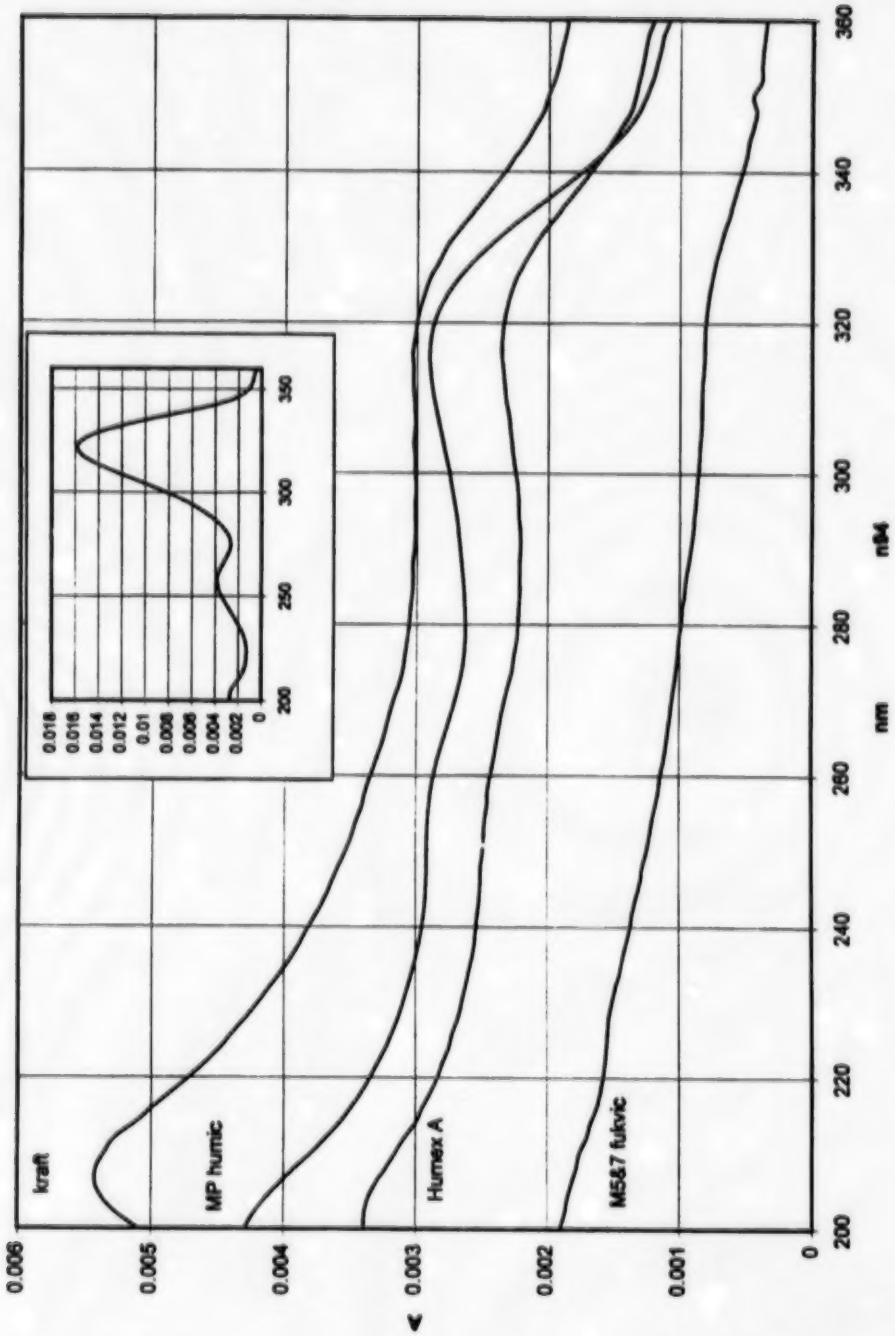


Fig. 11. Spectra of kraft lignin, Humex A, M5&M7 and MP humic NOM in concentrated sulfuric acid. Insert: spectrum of glucose.

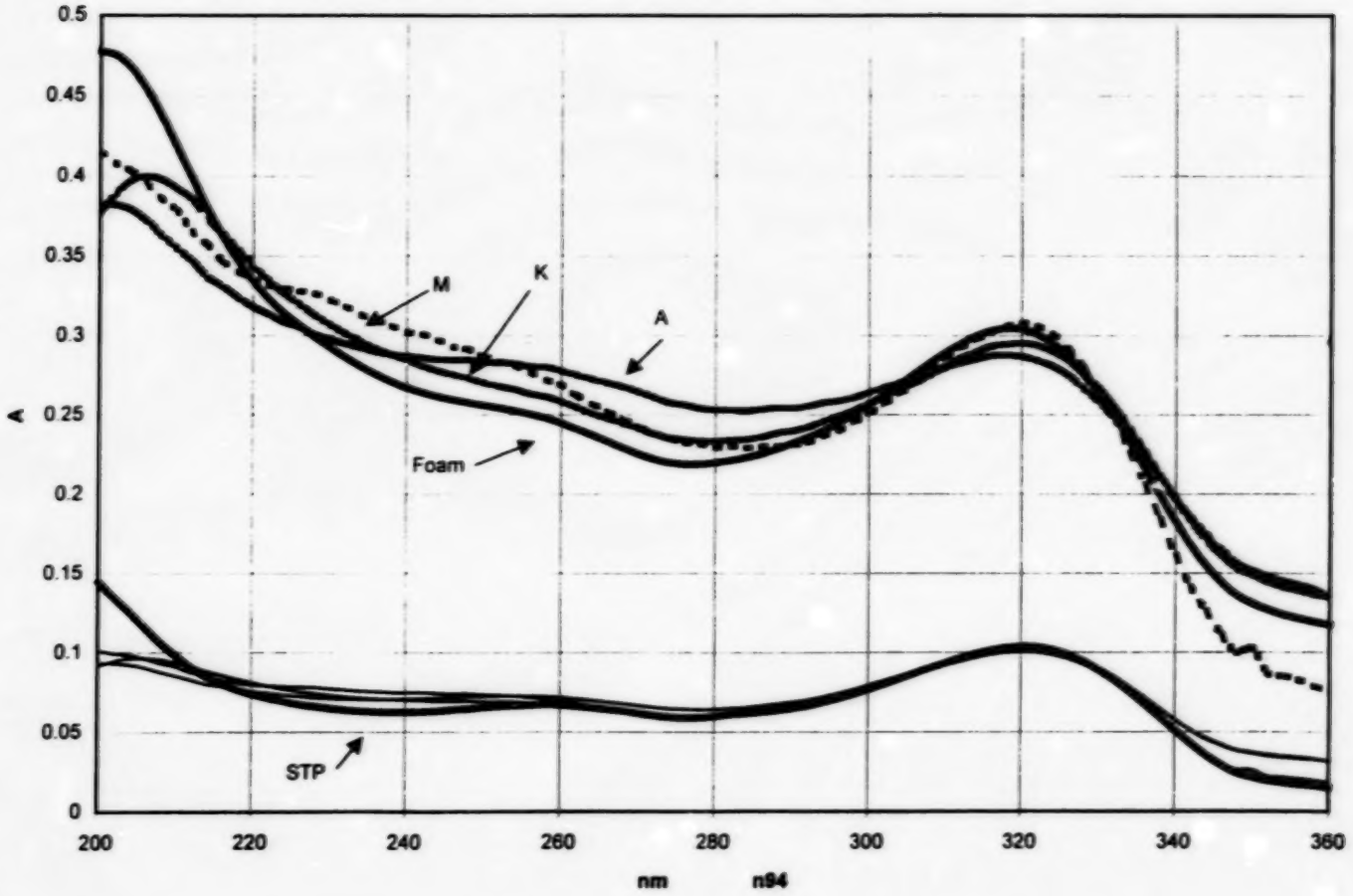


Fig. 12. Spectra of foam and STP effluent, and their approximations by glucose as a representative of a hexose polysaccharide, and M5&M7 NOM (M), kraft lignin (K), and Humex A (A).

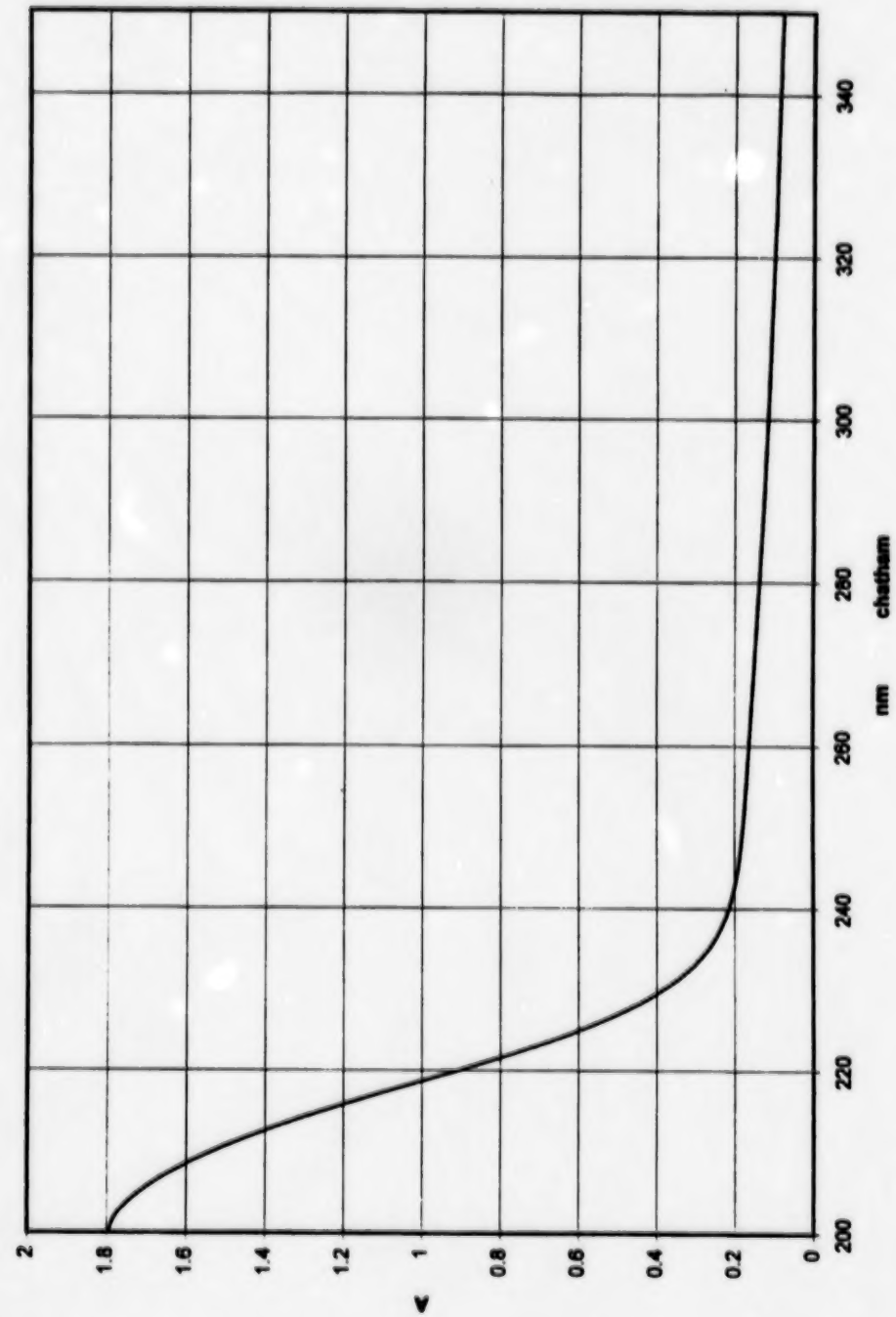


Fig. 13. Average spectrum of water from a Miramichi-East stream. A typical shape for nitrate, concentration 13.7 mg/L as $NO_3$.

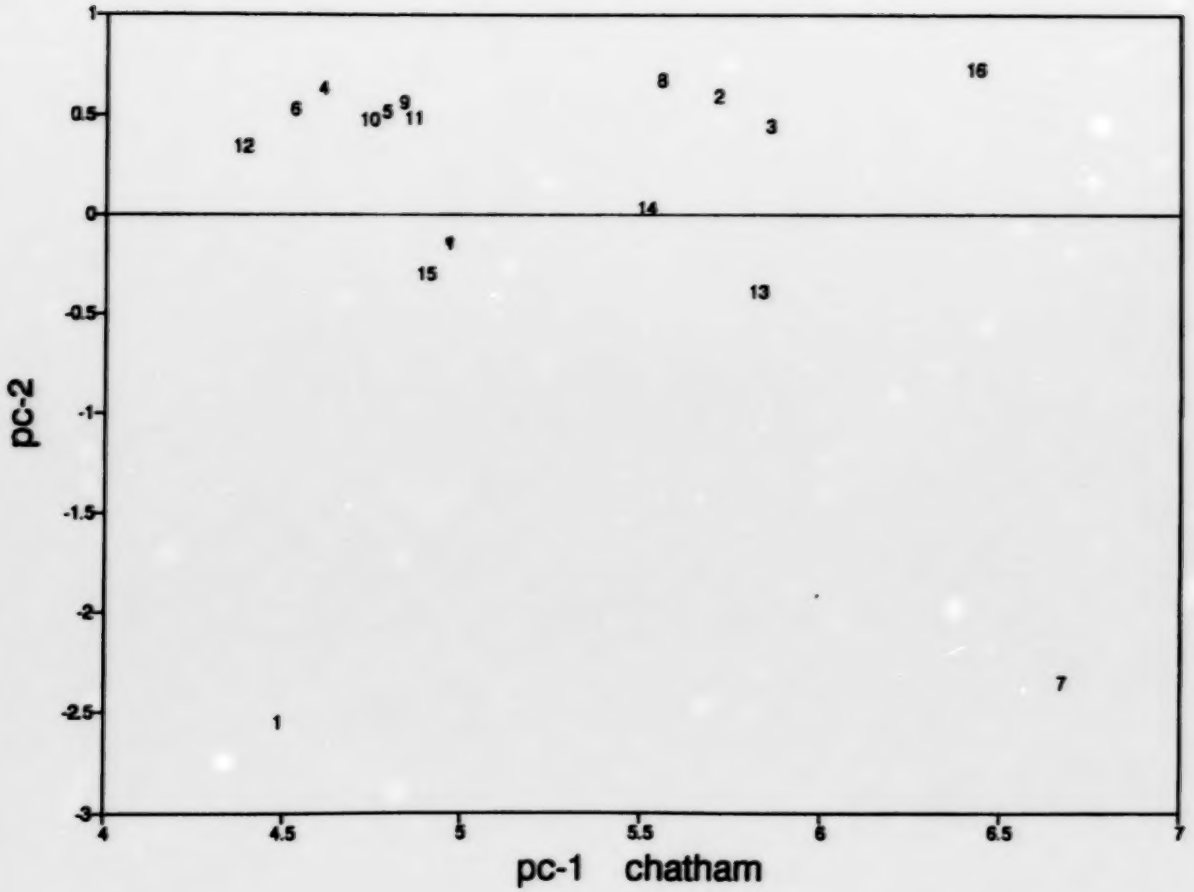


Fig. 14. Projection of spectra of water samples from a Miramichi-East stream, on the plane of the first two principal components. Proximity of samples indicates similarity. See Table 8 for sample identification.

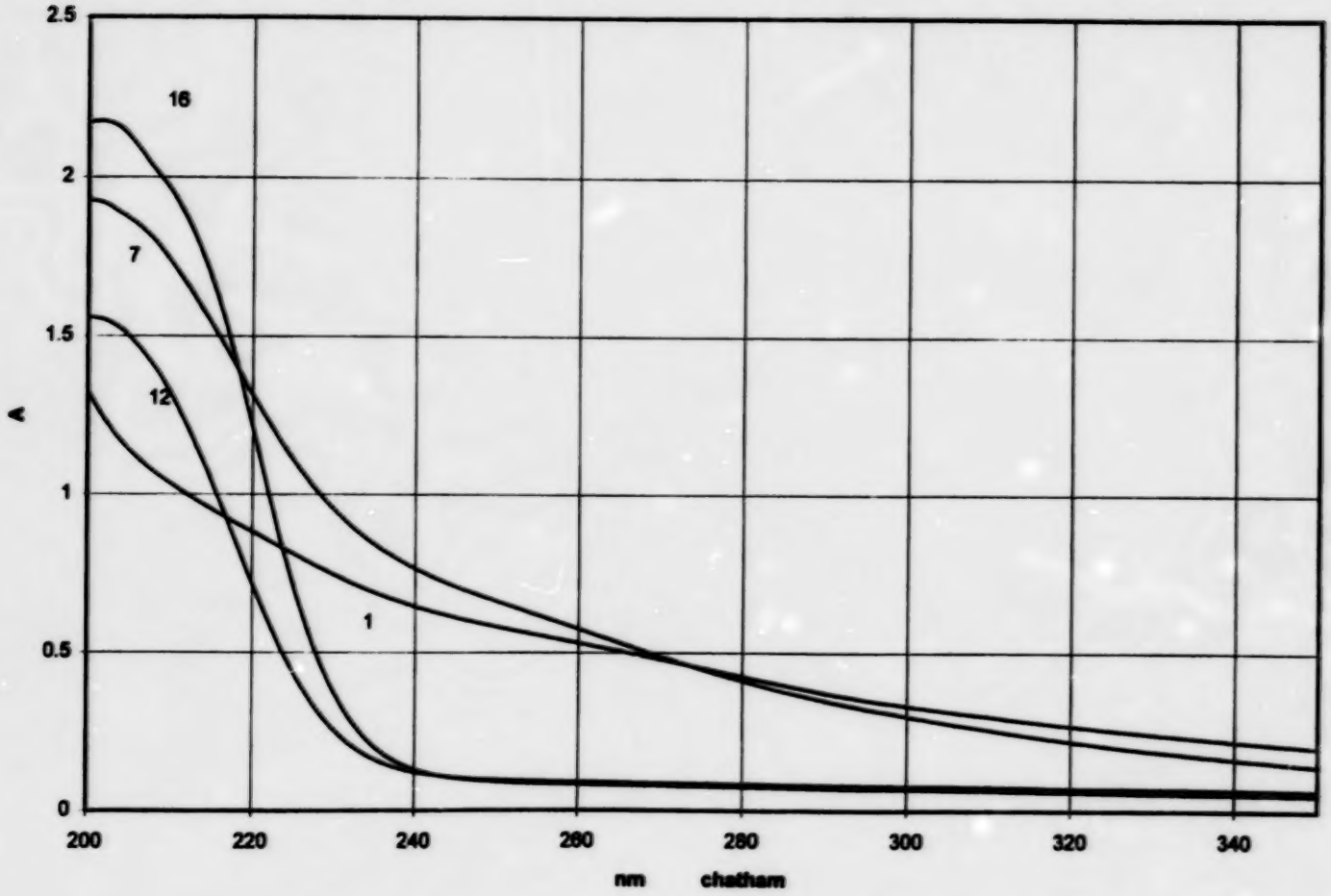


Fig.15. Spectra of the 'extreme' samples, indicated by the principal component projection (Fig.14).

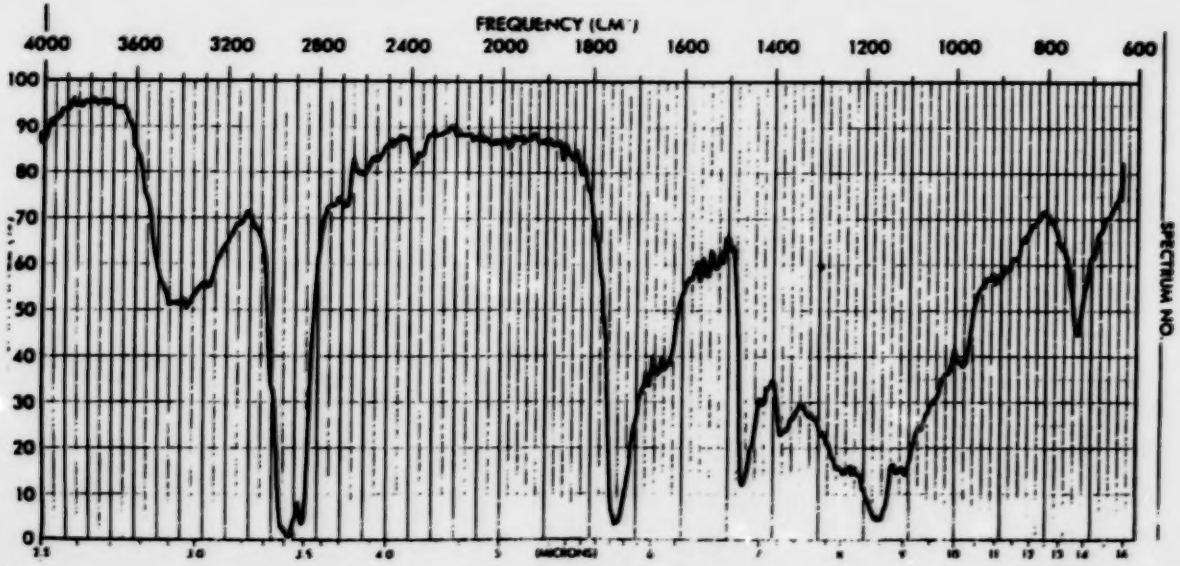


Fig.16. Infrared (IR) spectrum and a thin layer chromatogram (TLC) of dichloromethane extract of floating material. Both are typical of a rancid lipid. The large spot in the middle of TLC contained triglycerides, the streak from start on the left-hand side contained oxidation products, free fatty acids and, possibly, some phospholipids. The small spot on the right-hand side contained cholesterol.

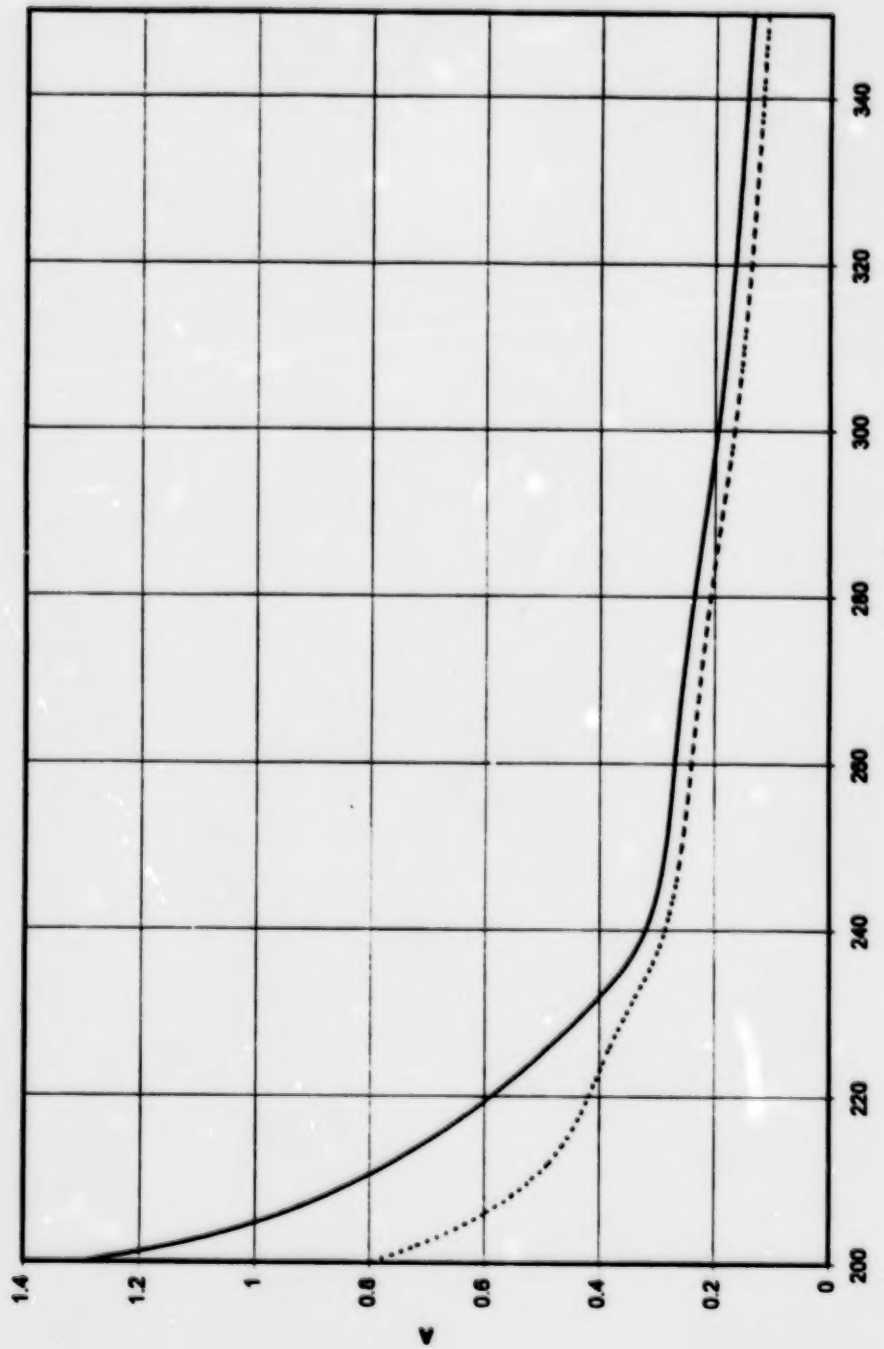


Fig.17 Spectra of the STP effluent, before (solid line) and after (dotted line) dialysis

# Appendix

Spectra of 80 samples form a table with 76 rows (wavelengths 200-350, step 2) and 80 columns. To save space, this table is presented as table A (76 rows, corresponding to wavelengths, by 8 columns) and table B (80 rows, corresponding to samples, by 8 columns). The original spectra may be reproduced by matrix multiplication of the matrix A (without the 1st column which contains the wavelengths), by the transposed (exchanged rows and columns) matrix B (without its 1st column which contains the sample codes). Average mean, median and maximum error of the reconstructed spectra is -5E-8, -5E-6, and 3E-3, respectively.

## A

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 200 | 14.6265771 | -2.1307605 | 1.16806361 | -0.2144152 | 0.25131897 | -0.1159455 | 0.02919618 | -0.0051955 |
| 202 | 13.8270873 | -2.3158558 | 0.55139045 | 0.06414265 | -0.1303552 | 0.10483454 | -0.067629 | 0.0141425 |
| 204 | 12.6320008 | -2.2411082 | -0.1460923 | 0.21474573 | -0.2561782 | 0.11491884 | 0.02948239 | -0.0101145 |
| 206 | 11.0466646 | -1.8433134 | -0.6950181 | 0.19806261 | -0.0969635 | -0.0405155 | 0.04165747 | -0.0048596 |
| 208 | 9.181462 | -1.1267634 | -0.8558509 | 0.07421162 | 0.09005021 | -0.1134592 | -0.0102973 | 0.00633101 |
| 210 | 7.37083175 | -0.3139349 | -0.7120504 | -0.0753539 | 0.15360993 | -0.0624459 | -0.0289774 | 0.00291684 |
| 212 | 5.90049883 | 0.36619373 | -0.4898715 | -0.1944113 | 0.14218779 | 0.01595717 | -0.0182744 | -0.0029227 |
| 214 | 4.83429102 | 0.84116337 | -0.3002258 | -0.2671893 | 0.1109607 | 0.07178763 | -0.0043236 | -0.0025254 |
| 216 | 4.11223707 | 1.13194149 | -0.1681912 | -0.3008824 | 0.07959439 | 0.0996671 | 0.00534259 | -0.0003576 |
| 218 | 3.63925536 | 1.29087253 | -0.082858 | -0.3077117 | 0.05204964 | 0.10402887 | 0.01134238 | 0.00232867 |
| 220 | 3.33303204 | 1.36451574 | -0.0316628 | -0.2972959 | 0.02988764 | 0.09335416 | 0.01297152 | 0.00633977 |
| 222 | 3.1277638 | 1.38686133 | -0.0010453 | -0.2781866 | 0.01007168 | 0.07685955 | 0.01315456 | 0.01020085 |
| 224 | 2.98433988 | 1.38360993 | 0.01679689 | -0.2556868 | -0.0055322 | 0.05611985 | 0.01192813 | 0.01035331 |
| 226 | 2.87480701 | 1.36502383 | 0.02698905 | -0.2333399 | -0.0187003 | 0.03837476 | 0.00821486 | 0.00841825 |
| 228 | 2.78402077 | 1.34070367 | 0.0332034 | -0.2106254 | -0.0273075 | 0.02309764 | 0.00525094 | 0.00289176 |
| 230 | 2.70398033 | 1.31368343 | 0.03756053 | -0.1881915 | -0.0340915 | 0.00926365 | 0.00064089 | -0.0045461 |
| 232 | 2.63018112 | 1.28529431 | 0.03913714 | -0.1671505 | -0.0393555 | -0.0018694 | -0.0042038 | -0.0108291 |
| 234 | 2.55929702 | 1.2583293 | 0.04027823 | -0.1469742 | -0.0423267 | -0.0114419 | -0.008035 | -0.0178977 |
| 236 | 2.49175984 | 1.23166588 | 0.03919398 | -0.127068 | -0.0463964 | -0.020675 | -0.010774 | -0.0225336 |
| 238 | 2.4265447 | 1.20596 | 0.03860816 | -0.1080635 | -0.0494094 | -0.0286992 | -0.010826 | -0.0234442 |
| 240 | 2.36487884 | 1.18242068 | 0.03669918 | -0.0905307 | -0.0526755 | -0.035603 | -0.0097758 | -0.0205464 |
| 242 | 2.3064507 | 1.16020714 | 0.03558038 | -0.0743444 | -0.053545 | -0.0410751 | -0.007767 | -0.0161505 |
| 244 | 2.25430988 | 1.1396411 | 0.03437757 | -0.0588433 | -0.0556196 | -0.047247 | -0.0047205 | -0.0104476 |
| 246 | 2.20818233 | 1.12077008 | 0.03308433 | -0.0448174 | -0.0563616 | -0.049818 | -0.0032071 | -0.0046992 |
| 248 | 2.16626509 | 1.10419777 | 0.0326637 | -0.0323255 | -0.0568739 | -0.0525772 | -0.0024969 | 0.00024308 |
| 250 | 2.13079697 | 1.08854594 | 0.03245743 | -0.0214822 | -0.0559117 | -0.0534246 | -0.0004651 | 0.003905 |
| 252 | 2.09943269 | 1.07562232 | 0.03220263 | -0.0127435 | -0.0548618 | -0.0541796 | -0.0002941 | 0.00659972 |
| 254 | 2.07078335 | 1.06225134 | 0.03237035 | -0.0043431 | -0.0536354 | -0.0529109 | 0.0008289 | 0.00855894 |
| 256 | 2.04193121 | 1.04836097 | 0.03253122 | 0.00336764 | -0.051123 | -0.0515778 | 0.00128945 | 0.01011165 |
| 258 | 2.01814722 | 1.03655719 | 0.03301589 | 0.01082238 | -0.0495887 | -0.0504879 | 0.00163017 | 0.01094519 |
| 260 | 1.99227748 | 1.02461353 | 0.03316779 | 0.01654112 | -0.047394 | -0.0477776 | 0.00209813 | 0.01157131 |
| 262 | 1.96501089 | 1.01104508 | 0.03385548 | 0.02343362 | -0.0449461 | -0.0456156 | 0.00192701 | 0.01206689 |
| 264 | 1.93826131 | 0.99680121 | 0.03420218 | 0.03065543 | -0.0422838 | -0.0426098 | 0.0017867 | 0.01178464 |
| 266 | 1.90953656 | 0.98170836 | 0.03538786 | 0.03805248 | -0.0394221 | -0.0391876 | 0.00194867 | 0.0113106 |
| 268 | 1.88090427 | 0.96737148 | 0.03544383 | 0.0443102 | -0.0356003 | -0.0351071 | 0.00220885 | 0.0112138 |
| 270 | 1.8511288 | 0.95196795 | 0.036034 | 0.05110107 | -0.0318177 | -0.0319264 | 0.00139757 | 0.00967262 |
| 272 | 1.82019488 | 0.93647412 | 0.03676467 | 0.05848656 | -0.0281685 | -0.0277786 | 0.00160444 | 0.00841138 |
| 274 | 1.78887769 | 0.92127131 | 0.03736154 | 0.06519521 | -0.0246257 | -0.0241805 | 0.00093227 | 0.00676196 |
| 276 | 1.75626311 | 0.90623791 | 0.03775429 | 0.07185932 | -0.0209023 | -0.0205584 | -4.787E-05 | 0.00521222 |
| 278 | 1.72487537 | 0.89082053 | 0.03857934 | 0.07858681 | -0.0168262 | -0.0166084 | -0.000238 | 0.00421657 |
| 280 | 1.69141839 | 0.8761058 | 0.0377288 | 0.08554625 | -0.0135669 | -0.013221 | -0.0003814 | 0.00250701 |
| 282 | 1.65828211 | 0.86226971 | 0.03830782 | 0.09219706 | -0.0100194 | -0.0106302 | -0.0008693 | 0.00177499 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 284 | 1.62581863 | 0.84783235 | 0.03805229 | 0.09879941 | -0.0070805 | -0.008029 | -0.0005554 | 0.00069679 |
| 286 | 1.59113495 | 0.83351775 | 0.03727695 | 0.10501414 | -0.0047737 | -0.0065672 | -0.0008859 | -0.0004008 |
| 288 | 1.55679841 | 0.81865262 | 0.03644756 | 0.11152396 | -0.0017977 | -0.0053417 | -0.000556 | -0.0003913 |
| 290 | 1.522167 | 0.80499543 | 0.03487806 | 0.11852892 | 0.00058495 | -0.0033201 | -0.0002671 | -0.0007595 |
| 292 | 1.48815612 | 0.79164694 | 0.03351856 | 0.1257134 | 0.00338895 | -0.0029644 | 6.8472E-05 | -0.0001587 |
| 294 | 1.45524519 | 0.77846594 | 0.0322973 | 0.13243073 | 0.00537561 | -0.0014601 | 0.00051212 | -0.0004017 |
| 296 | 1.42434986 | 0.76491812 | 0.03146803 | 0.13848529 | 0.00828634 | -0.0008057 | 0.0004927 | -0.000271 |
| 298 | 1.39453394 | 0.75273878 | 0.03054741 | 0.1449035 | 0.01012152 | 0.00037709 | 0.00060095 | -0.0006135 |
| 300 | 1.36539613 | 0.73926534 | 0.02908928 | 0.15127201 | 0.01263784 | 0.00181017 | 0.00056251 | -0.0012583 |
| 302 | 1.34038458 | 0.72779998 | 0.02881244 | 0.15707418 | 0.0144194 | 0.00299031 | 0.00019496 | -0.0021561 |
| 304 | 1.31388871 | 0.71555334 | 0.02859655 | 0.16190306 | 0.01620687 | 0.0040994 | 0.00086008 | -0.0018528 |
| 306 | 1.28739306 | 0.70430644 | 0.02768899 | 0.16771359 | 0.01869132 | 0.00555898 | 0.00063364 | -0.0029605 |
| 308 | 1.26374788 | 0.69316721 | 0.02674139 | 0.17346831 | 0.0202466 | 0.00741061 | 0.00021622 | -0.0025918 |
| 310 | 1.24152282 | 0.68155352 | 0.02704834 | 0.17856253 | 0.02298617 | 0.00879821 | -2.978E-07 | -0.0033623 |
| 312 | 1.21908757 | 0.67087745 | 0.0264632 | 0.18466247 | 0.02458039 | 0.01010133 | 0.00022002 | -0.0034455 |
| 314 | 1.19776347 | 0.66043399 | 0.02585747 | 0.188956 | 0.02659262 | 0.01152623 | -0.000132 | -0.0037169 |
| 316 | 1.17641845 | 0.65036573 | 0.02629652 | 0.19451652 | 0.0285471 | 0.01333132 | 4.8866E-05 | -0.003452 |
| 318 | 1.15576892 | 0.63978052 | 0.02497436 | 0.19897996 | 0.02998031 | 0.0146571 | 0.000548 | -0.0036449 |
| 320 | 1.13546799 | 0.63076528 | 0.0243004 | 0.20344049 | 0.03202553 | 0.01568389 | 0.00031673 | -0.00314 |
| 322 | 1.11632361 | 0.62078585 | 0.02475068 | 0.20829445 | 0.03399081 | 0.01797929 | 0.00013041 | -0.0031239 |
| 324 | 1.09653499 | 0.61150478 | 0.02428422 | 0.21291564 | 0.03570929 | 0.01919793 | -0.0001682 | -0.0034218 |
| 326 | 1.07654514 | 0.60263211 | 0.02410432 | 0.21744161 | 0.03733294 | 0.02057649 | 2.8729E-05 | -0.0027338 |
| 328 | 1.05801109 | 0.5931364 | 0.02339481 | 0.22163597 | 0.03890345 | 0.022223 | 3.6999E-05 | -0.0026138 |
| 330 | 1.03930721 | 0.58525266 | 0.02354842 | 0.22583861 | 0.04085412 | 0.02364814 | 3.5615E-06 | -0.002351 |
| 332 | 1.02065534 | 0.57598547 | 0.02288546 | 0.2293864 | 0.04240169 | 0.025045 | 0.00041833 | -0.0020792 |
| 334 | 1.00295968 | 0.56746027 | 0.02286882 | 0.23382114 | 0.0432239 | 0.02637101 | 0.00039064 | -0.0014058 |
| 336 | 0.98647355 | 0.55951401 | 0.0228915 | 0.23680074 | 0.04487597 | 0.02715546 | 0.00049057 | -0.0007891 |
| 338 | 0.96734388 | 0.55092474 | 0.02248136 | 0.24074199 | 0.04589856 | 0.02915532 | 0.00016532 | -0.000337 |
| 340 | 0.95277686 | 0.54280726 | 0.02199097 | 0.24430192 | 0.04777505 | 0.03046626 | 0.00056728 | 0.00053916 |
| 342 | 0.93758048 | 0.53461469 | 0.02159555 | 0.24763181 | 0.04930616 | 0.03107632 | 0.00074935 | 0.00043857 |
| 344 | 0.9217734 | 0.52618431 | 0.02214112 | 0.25157144 | 0.0504718 | 0.0326933 | 0.00044324 | 0.00091443 |
| 346 | 0.90798147 | 0.51902292 | 0.02195025 | 0.25463875 | 0.05139139 | 0.03444329 | 0.00071013 | 0.00168811 |
| 348 | 0.8912582 | 0.50923072 | 0.02177688 | 0.25487992 | 0.05198708 | 0.03435213 | 0.00043859 | 0.00141855 |
| 350 | 0.86969107 | 0.50001583 | 0.02140701 | 0.25707572 | 0.05393212 | 0.03507249 | 0.0008274 | 0.00129163 |

**B**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 1a | 0.13076078 | -0.1361881 | -0.1752876 | 0.03748439 | 0.20103722 | -0.1375079 | -0.1924132 | 0.07449823 |
| 1b | 0.12883083 | -0.1388109 | -0.1636899 | 0.04818381 | 0.16621212 | -0.1405091 | -0.1861072 | 0.08271591 |
| 2a | 0.1311501 | -0.1190931 | -0.1192163 | 0.04156399 | 0.07234263 | -0.060843 | 0.06427467 | -0.0229643 |
| 2b | 0.13345676 | -0.1219409 | -0.1586081 | 0.01602316 | 0.12801647 | -0.0795361 | -0.1239051 | 0.02627319 |
| 3a | 0.13239863 | -0.1223558 | -0.1483776 | 0.02404935 | 0.107381 | -0.1093858 | -0.0949193 | 0.02374952 |
| 3b | 0.13186513 | -0.1210243 | -0.1363929 | 0.03399065 | 0.08402478 | -0.1118659 | -0.0755617 | 0.01731153 |
| 4a | 0.1314709 | -0.1218332 | -0.1265365 | 0.02941006 | 0.08038643 | -0.1174697 | -0.0096891 | -0.0088061 |
| 4b | 0.13188147 | -0.1211858 | -0.143327 | 0.02812173 | 0.07718021 | -0.0941532 | -0.0640195 | 0.02085442 |
| 5a | 0.13494346 | -0.0832342 | -0.0492402 | 0.00339538 | -0.0679817 | 0.0436687 | 0.1125619 | -0.0358996 |
| 5b | 0.1326118 | -0.0904319 | -0.0418056 | 0.03063827 | -0.0887255 | 0.00316318 | 0.13067141 | -0.0618423 |
| 6a | 0.13538427 | -0.0954889 | -0.0913884 | 0.00435075 | -0.0034044 | -0.0088781 | 0.09365038 | -0.0233535 |
| 6b | 0.13513296 | -0.0983329 | -0.1045267 | 0.00514308 | 0.00766117 | -0.0185773 | 0.12434948 | -0.0385802 |
| 7a | 0.13384945 | -0.0786042 | -0.0089766 | 0.03162546 | -0.0825765 | 0.00814036 | 0.21238024 | -0.1235739 |
| 7b | 0.1303185 | -0.0878389 | -0.0038554 | 0.04034855 | -0.1100102 | 0.05492492 | 0.15354689 | -0.0457653 |
| 8a | 0.13145774 | -0.058698 | 0.06065097 | 0.03407377 | -0.1220292 | 0.08356217 | 0.09926541 | -0.0832015 |
| 8b | 0.12972971 | -0.073591 | 0.04104632 | 0.02107277 | -0.1097865 | 0.08901702 | 0.15399503 | -0.0755322 |
| 9a | 0.12700364 | -0.0660456 | 0.08839035 | 0.02026575 | -0.1132283 | 0.07740411 | 0.03693457 | -0.0021205 |
| 9b | 0.12841236 | -0.0633284 | 0.07727503 | 0.00219735 | -0.1274519 | 0.0831396 | -0.0123342 | -0.0283372 |
| 10a | 0.12755798 | -0.0595126 | 0.09472284 | 0.03080323 | -0.125223 | 0.09697936 | -0.0075495 | 0.01655947 |
| 10b | 0.12752371 | -0.0678671 | 0.08219515 | 0.02287645 | -0.1139836 | 0.07872912 | 0.0239296 | 0.00912634 |
| 11a | 0.15517173 | 0.0523211 | 0.12322268 | 0.33355663 | 0.04602255 | 0.18680091 | 0.03984237 | -0.0627662 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 11b | 0.12637681 | -0.0536349 | 0.11824593 | 0.02570632 | -0.1099663 | 0.07466944 | -0.0869568 | 0.08740824 |
| o611a | 0.1409669 | 0.14200278 | 0.09368849 | -0.1356427 | 0.03820958 | -0.1386162 | 0.03999773 | -0.0876186 |
| o611b | 0.14474423 | 0.13836845 | 0.10577834 | -0.1233105 | 0.0365119 | -0.1343199 | -0.0353478 | -0.0453968 |
| 12a | 0.12692771 | -0.0422814 | 0.12701081 | -0.0042874 | -0.1001378 | 0.09732879 | -0.2018595 | 0.10844014 |
| 12b | 0.12726015 | -0.0495671 | 0.11660615 | -0.0055362 | -0.0886379 | 0.09216958 | -0.0604548 | 0.01477473 |
| 13a | 0.11848289 | -0.008709 | 0.18997799 | -0.0439949 | 0.08790779 | 0.05065478 | -0.1406317 | -0.0135524 |
| 13b | 0.11555461 | -0.0254623 | 0.21226529 | -0.0222923 | 0.02861841 | 0.00432069 | -0.2345011 | 0.14995744 |
| 14a | 0.12516368 | -0.0457265 | 0.13296202 | -0.0214814 | -0.1001026 | 0.07767793 | -0.1965199 | 0.08151158 |
| 14b | 0.13730489 | 0.0141123 | 0.16318816 | 0.15603994 | -0.0217592 | 0.11010384 | -0.229517 | 0.08301943 |
| o614a | 0.13838608 | 0.14807973 | 0.08843257 | -0.142612 | 0.02914754 | -0.1725697 | 0.06759184 | -0.0681833 |
| o614b | 0.13784471 | 0.15160236 | 0.08661699 | -0.1404494 | 0.03622829 | -0.1776685 | 0.1141942 | -0.1089118 |
| 15a | 0.09227587 | -7.685E-05 | 0.24072253 | -0.039033 | 0.18302352 | -0.1518477 | 0.07288615 | 0.04017006 |
| 15b | 0.10344162 | -0.0137958 | 0.24473303 | -0.0558795 | 0.12215239 | -0.1008396 | -0.1061648 | 0.09327088 |
| 16a | 0.13493919 | 0.03788657 | 0.12053847 | -0.1135636 | 0.10022447 | 0.149833 | -0.2513261 | -0.1993785 |
| 16b | 0.13060956 | 0.00877527 | 0.14163079 | -0.0782083 | 0.04243805 | 0.1237878 | -0.2633086 | 0.02998509 |
| 17a | 0.1066571 | 0.05162975 | 0.17739004 | -0.0500041 | 0.16077227 | -0.1140474 | 0.12088839 | 0.0392516 |
| 17b | 0.11037985 | 0.05035717 | 0.18782072 | -0.0497582 | 0.15755073 | -0.1152532 | 0.09693953 | 0.00989741 |
| 18a | 0.08381085 | 0.04098715 | 0.17691019 | -0.0460035 | 0.16114748 | -0.1790753 | 0.17393418 | -0.0788629 |
| 18b | 0.08617804 | 0.03734604 | 0.18855259 | -0.0436863 | 0.17171776 | -0.1825149 | 0.19123087 | -0.0741667 |
| 19a | 0.07822176 | 0.15013328 | -0.070602 | -0.0787251 | -0.0610843 | -0.0383492 | -0.0003694 | -0.0482533 |
| 19b | 0.0770374 | 0.139778 | -0.072568 | -0.0850577 | -0.0342517 | -0.0080567 | 0.01667135 | 0.07214177 |
| 20a | 0.1164721 | 0.32881118 | -0.0658743 | 0.45423195 | 0.09213346 | 0.03543537 | 0.00323839 | -0.0853338 |
| 20b | 0.07391822 | 0.14655412 | -0.1018726 | -0.0802505 | -0.0570359 | 0.02185281 | -0.0316085 | 0.07435685 |
| o520a | 0.0683637 | 0.1375241 | -0.0942956 | -0.0926312 | -0.0857166 | -0.0115147 | -0.0393557 | 0.07438145 |
| o520b | 0.06826645 | 0.13913059 | -0.0915124 | -0.0914462 | -0.0915428 | -0.0215681 | -0.0357177 | 0.05714985 |
| o620a | 0.0635879 | 0.1354262 | -0.0795577 | -0.0691207 | -0.0962742 | -0.0347327 | -0.0493065 | -0.0415345 |
| o620b | 0.06436485 | 0.1369153 | -0.0808211 | -0.0699372 | -0.0965874 | -0.0338537 | -0.0398476 | -0.0445141 |
| 21a | 0.04536649 | 0.08580748 | -0.0094405 | 0.00843212 | -0.0016889 | -0.0495686 | 0.02792829 | 0.02748057 |
| 21b | 0.05248559 | 0.06549028 | 0.05117048 | -0.0124187 | 0.06748089 | -0.0918375 | 0.12223393 | -0.0127008 |
| 22a | 0.09621284 | 0.29174522 | -0.0277781 | 0.47854003 | 0.06842459 | -0.0493533 | -0.0142716 | 0.01619289 |
| 22b | 0.08082874 | 0.21570762 | -0.0438153 | 0.31765524 | 0.09897475 | 0.05551799 | -0.0058335 | -0.0492814 |
| o522a | 0.04191471 | 0.08257388 | -0.0489075 | -0.0427333 | -0.0374481 | -0.0066448 | -0.013903 | 0.04008299 |
| o522b | 0.04224107 | 0.08212695 | -0.0505053 | -0.0452301 | -0.0372294 | -0.0033116 | -0.0147797 | 0.04808732 |
| o622b | 0.08924092 | 0.19000878 | -0.1210517 | -0.1153124 | -0.1436242 | -0.0445986 | -0.0646512 | -0.0246675 |
| o822a | 0.08851442 | 0.1871234 | -0.1194294 | -0.1102135 | -0.1331775 | -0.0344182 | -0.0569291 | -0.0262061 |
| o822b | 0.08991248 | 0.18980377 | -0.1218852 | -0.1144913 | -0.13484 | -0.0311873 | -0.0608658 | -0.0502368 |
| 23a | 0.04188472 | 0.08815058 | -0.0419863 | -0.0161387 | -0.0399633 | -0.0195424 | -0.0112693 | 0.04380561 |
| 23b | 0.04291526 | 0.08899379 | -0.0472043 | -0.0365775 | -0.0557936 | -0.0252139 | -0.0245696 | 0.02289944 |
| 25a | 0.04225977 | 0.08850721 | -0.0427961 | -0.018238 | -0.0389974 | -0.0151731 | -0.0094386 | 0.04546689 |
| 25b | 0.04732272 | 0.0983424 | -0.0512448 | -0.0314681 | -0.0476205 | -0.0172739 | -0.0141779 | 0.04662103 |
| on1s | 0.1343478 | -0.0744042 | -0.0133833 | 0.01113777 | -0.1277741 | 0.02288583 | 0.06584575 | 0.02997214 |
| on2s | 0.13609546 | -0.069781 | -0.0206021 | 0.00536146 | -0.1122903 | 0.02376078 | 0.13621427 | -0.0121702 |
| on3n | 0.13479746 | -0.0704913 | -0.0064826 | 0.00689073 | -0.1273047 | 0.03307537 | 0.13715909 | -0.0308324 |
| on4n | 0.13572651 | -0.0699319 | -0.0150667 | 0.01241429 | -0.1060759 | 0.01815411 | 0.161444 | -0.0322703 |
| mi1s | 0.1348513 | -0.1109589 | -0.147476 | 0.01368346 | 0.06730465 | -0.0853357 | -0.0979887 | 0.0835065 |
| mi2s | 0.13469857 | -0.1040032 | -0.1177144 | 0.02263131 | 0.01704862 | -0.0806529 | 0.07187139 | 0.01915873 |
| mi3n | 0.13419744 | -0.1040219 | -0.1091872 | 0.01853137 | 0.01951927 | -0.0810564 | 0.01056097 | 0.04378354 |
| mi4n | 0.13446826 | -0.1069128 | -0.1296173 | 0.01680446 | 0.03352656 | -0.0847891 | -0.034758 | 0.06046923 |
| cc1 | 0.13477558 | -0.0540785 | 0.03936627 | -0.0082277 | -0.1436761 | 0.06087954 | 0.02950387 | 0.00988754 |
| cc2 | 0.13429305 | -0.0437428 | 0.06231512 | -0.016892 | -0.1497079 | 0.08087235 | -0.0171335 | -0.016425 |
| cc3 | 0.14360323 | -0.0503934 | -0.0502743 | 0.04405999 | -0.0932295 | 0.0151139 | 0.069496 | -0.0337379 |
| m1 | 0.03973026 | 0.07263074 | -0.0424 | -0.0295423 | -0.0004874 | 0.02452884 | -0.0029321 | 0.03159542 |
| m2 | 0.07887539 | 0.14517146 | -0.1002115 | -0.1209142 | -0.0572385 | 0.01555872 | -0.0162557 | 0.14458451 |
| m3 | 0.04867892 | 0.08283565 | -0.0617178 | -0.056633 | 0.01337892 | 0.05492886 | -0.0025977 | 0.11087154 |
| m5 | 0.04462592 | 0.07992503 | -0.0494814 | -0.0573129 | -0.0211058 | 0.00933789 | -0.0071587 | 0.09758382 |
| m6 | 0.0685847 | 0.13666197 | -0.0849403 | -0.0541453 | -0.0497238 | 0.00818813 | -0.018129 | 0.08918061 |
| m7 | 0.0419994 | 0.0843885 | -0.046736 | -0.0414848 | -0.0481206 | -0.0170428 | -0.0194075 | 0.04699721 |
| foam | 0.11568215 | 0.0378902 | -0.1951896 | -0.2397628 | 0.38780571 | 0.47761752 | -0.0666718 | -0.5633275 |
| stp | 0.10368998 | 0.0975222 | -0.0737236 | -0.1478391 | 0.35957023 | 0.46212053 | 0.34584143 | 0.59734353 |